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PERFORMANCE EVALUATION OF FULL-SCALE HAZARDOUS WASTE INCINERATORS

VOLUME II

INCINERATOR PERFORMANCE RESULTS

by

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16. ABSTRACT

This report is Volume II, Incinerator Performance Results, of a series of extensive performance data EPA obtained through eight (8) field tests of actual industrial/ commercial incinerators, was prepared in response to the Agency's need to conduct a regulatory impact analysis (RIA) for hazardous waste incinerators to determine the need, adequacy, and economic feasibility of current RCRA incinerator regulations. Tests involved trial burn-type testing at each plant during typical albeit closely monitored daily operations on wastes typical of their routine disposal function.

Most incinerators were found to be closely approaching or performing within RCRA requirements for destruction of compounds, although some facilities showed substandard results in other areas.

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FOREWORD

When energy and material resources are extracted, processed, converted, and used, the related pollutional impacts on our environment and even on our health often require that new and increasingly more efficient pollution control methods be used. The Industrial Environmental Research Laboratory-Cincinnati (IERL-Ci) assists in developing and demonstrating new and improved methodologies that will meet these needs both efficiently and economically.

This report is one of a five-volume series of reports presenting the recent testing and evaluation results of the performance of eight (8) commercial and industrial hazardous waste incinerators. The Agency's purpose was to gather accurate data on full-scale incinerator environmental performance, for the EPA's use in developing a regulatory impact analysis document in the near future for all such incinerators subject to existing RCRA standards. Because the performance information contained herein is of high interest to the hazardous waste incineration technical community in general, EPA wishes to make it available as a technical report at this time.

The material contained in this report has been reviewed and approved by experts within the Agency with state-of-the-art knowledge of the operation, testing, and evaluation of incinerator performance. During sampling and analysis of the incinerators in the field, EPA's most modern and scientific methods were employed along with the appropriate level of quality assurance and quality control. The incinerators were studied during a closely monitored mode of operation while disposing of mixtures of real-world hazardous wastes typical of their usual feedstocks. We are pleased to report that under these circumstances the incinerators were generally successful in performing their task of safely destroying hazardous waste and controlling other harmful emissions to the environment with some exceptions.

Requests for further information regarding this report on performance of full-scale incineration facilities should be directed to the Energy Pollution Control Division, IERL, Cincinnati.

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ABSTRACT

This report describes a study to evaluate current baseline performance of hazardous waste incinerators. Tests were conducted at eight full scale facilities to characterize all feed and effluent streams. Pollutants measured included EPA Appendix VIII hazardous compounds, particulates, hydrogen chloride, carbon monoxide, and total hydrocarbons. The data were analyzed to address questions on Destruction and Removal Efficiency (DRE), products of incomplete combustion (PIC), pollutant emission levels, performance of air pollution control systems, and relationships of process parameters to destruction efficiency and emission levels. A large base of data on performance of hazardous waste incinerators was accumulated, and many possible relationtionships between parameters were explored. Conclusions included: DREs were generally above 99.99%; measured DREs tended to be higher when concentration of the hazardous compound in the waste was higher; the most frequently observed PICs were benzene, toluene, chloroform, tetrachloroethylene, and naphthalene; the particulate EPA regulation of 180 mg/Nm^3 was not routinely met; and the hydrogen chloride EPA regulation almost always met.

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The cooperation of all test sites and the efforts of many individuals in Midwest Research Institute's Environmental Systems and Analytical Chemistry Departments are also acknowledged.

SECTION 1.0

INTRODUCTION

The Environmental Protection Agency's (EPA's) Office of Solid Waste is required under Executive Order 12291 to conduct a Regulatory Impact Analysis (RIA) that will ascertain the costs and benefits associated with various approaches to regulating hazardous waste incinerators. An integral step in this process is the evaluation of the destruction of hazardous organic pollutants in incinerators with different designs, operating conditions, and waste feed characteristics, and of the effectiveness of control devices for the removal of particulate and HCl emissions. This study of eight hazardous waste incinerators contributed to a compilation of a data base which will be used in characterizing incinerator performance.

The goal of this study was to establish current baseline levels of performance for incinerators through measurement of pollutant emissions at the selected set of incinerators and to analyze the data for performance trends. EPA chose eight incinerators with a variety of waste feeds, combustion chamber designs, operating conditions, and control equipment. This report presents a series of "snapshots" depicting good performance for those eight incinerators. Any existing operating problems were usually corrected prior to the tests.

The primary measures of performance examined during this program were destruction and removal efficiency (DRE) for primary organic hazardous constituents (POHCs) and removal of HCl and particulates from the stack gases, as described in the hazardous waste incinerator regulations (40 CFR 264, Subpart O, Sections 264.340-264.351). Additional parameters measured at one or more sites during the program included POHCs in liquid and solid effluents (e.g., ash and scrubber waters), products of incomplete combustion (PICs) in the stack gas, metals content in ash and particulate, and the effect of control devices on DRE. Standard EPA sampling and analysis methods were used where applicable, but other state-of-the-art techniques were evaluated and used as necessary. Experience with the sampling and analysis methods was reviewed, and the entire body of data was scrutinized for information which might be useful in a regulatory impact assessment or to further studies of incineration. Analyses of the data collected were directed toward documenting specific observations for sampling and analysis methods, identifying impacts of particular incineration conditions, and developing general conclusions on incinerator performance from data gathered throughout the program. As a result, this report adds a substantial amount of data to existing information on full-scale incinerators.

To properly interpret the results of this study, several caveats are important. First, this study was not intended to thoroughly document the relationships between incinerator designs and destruction of hazardous constituents. A rigorous experimental matrix of incineration parameters was not used nor were detailed facility characterizations prepared. Instead, the facilities were examined under normal operations with the fewest possible changes in typical operating conditions. As a result, the report does not provide a complete characterization of incinerator performance for specific POHCs under varied operating conditions. Second, the tests conducted were not official trial burns, although they did include all of the sampling and analysis normally required for trial burns. Third, new sampling and analysis procedures were evaluated during the study. However, the study was not a methods development study, and the conclusions regarding sampling and analysis procedures should be interpreted accordingly.

The remainder of Volume II is divided into three sections. First, a brief summary of the conclusions reached as a result of this study and a list of recommendations for further work in this area are presented. Second, a program description reviews the general structure of the sampling and analysis program and provides an overview of the facilities tested. Finally, the results section discusses organic emissions, control of chloride and particulate emissions, quality of results, and experience with sampling and analysis. This volume presents a summary of the data collected and the results of the data analysis. In addition, an extensive set of appendices are presented in Volumes III through V to compile and document sampling and analysis methods and protocols, individual test reports for each of the sites, and quality assurance/quality control efforts. A summary of the program activities and results is presented in Volume I, Executive Summary.

SECTION 2.0

CONCLUSIONS AND RECOMMENDATIONS

Through a series of sampling and analysis activities and extensive data evaluation, this program provided insight to the performance of hazardous waste incinerators. In addition, the program greatly increased information on the intricacies of incinerator sampling and analysis. Conclusions related to the performance of hazardous waste incinerators as measured by organic emissions (DRE of POHCs and formation of PICs), particulate emissions, and HCl emissions are presented in Section 2.1, as are conclusions related to sampling analysis.

While some significant conclusions were developed, the program did not completely characterize incinerator performance. Recommendations for future work are presented in Section 2.2. Recommendations or cautions related to future incinerator testing are also presented in Section 2.2.

2.1 CONCLUSIONS

1. Extensive analysis of organic emissions data provided the following insight into the factors affecting Destruction and Removal Efficiency (DRE):

- DREs for the incinerators tested were generally above 99.99%.
- DRE appears to be strongly correlated to concentration of the POHC in the waste feed. POHCs at higher waste feed concentrations were observed to be destroyed or removed to a higher degree. The phenomena that caused this relationship was not identified
- Analyses of data collected on this program showed no clear correlation between DRE and heat of combustion for POHCs.
- Data compiled from the eight tests were not sufficient to define parametric relationships between residence time, temperature, heat input, or O_2 concentration and DRE.
- The data from the eight tests suggest that POHC levels in scrubber water and ash were generally very low or nondetectable. These data suggest that the majority of POHCs are destroyed rather than merely transferred to another media in the incineration process.

- Some Appendix VIII compounds detected in the stack (primarily trihalomethanes) appear to be stripped from the scrubber water by the hot stack gas. Trihalomethanes detected in the scrubber inlet water were not detected in the effluent water. The effect can be lower measured/calculated DREs even though the destruction mechanisms may not be affected.

2. Evaluation of organic emissions data for compounds classified as Products of Incomplete Combustion (PICs are defined on this program as Appendix VIII compounds detected in the stack, which were not found in the waste feed in concentrations above 100 μg/g) led to the following observations:

- Stack gas concentrations of PICs were typically as high as or higher than those for POHC compounds in the stack.

- PIC output rate infrequently exceeded 0.01% of POHC input rate. (The 0.01% criteria was proposed in FR Vol. 45, No. 197, October 8, 1980.)

- The three likely mechanisms that explain the presence of most PICs are:

  a. Poor DREs for Appendix VIII compounds present at low concentration (< 100 μg/g) in the waste feed;

  b. Input of POHCs to the system from sources other than waste feed (e.g., scrubber water); and

  c. Actual incomplete combustion products or complex side reactions including recombination.

- Data from the tests suggest that benzene, toluene, chloroform, tetrachloroethylene, and naphthalene have a high potential for appearing as by-products of the combustion of organic wastes.

3. Compliance with the particulate standard of 180 mg/Nm^3 was not achieved at half of the sites tested. Particulate control devices were operated at five of the eight facilities and two of these five failed to achieve the standard. Two of the three facilities without control devices also failed the particulate standard. Data from this study suggest that any facility firing wastes with ash content greater than 0.5% will need a particulate control device to meet the standard.

4. Carbon monoxide (CO) and total hydrocarbons (THC) were monitored on a continuous basis to assess their utility as indicators of incinerator performance. The analysis indicates that CO and THC may provide indication of changes in incinerator performance and gross malfunctions in the combustion process. However, under the conditions of these tests CO and THC levels did not appear to be good predictors of POHC emissions or DRE, either across the plants tested or at a specific site, for DREs in the vicinity of 99.99%. It should also be pointed out that these tests were not conducted

in a parametric fashion specifically designed to determine if such a correlation could be found.

5. HCl emissions were generally easily controlled to meet one of the two criteria specified in the regulations--less than 1.8 kg HCl/hr or greater than 99% removal efficiency.

6. Of the six sites that were tested for chlorinated dioxins and chlorinated furans, dioxins were found at one site and furans were found at three sites. No 2,3,7,8-TCDD was detected. The maximum concentrations detected were 0.06 ng/L of chlorinated furans and 0.02 ng/L of chlorinated dioxins.

7. A Volatile Organic Sampling Train (VOST) was developed and used during these tests. The VOST method provided a consistent and reliable data base when operated by personnel familiar with the apparatus and procedures. Proper use of these procedures was critical to obtaining reliable data.

8. Two methods were used on this program for sampling volatile organics in the stack--VOST and gas bags. When these two methods are compared, VOST provided better data on this program. The VOST method provided lower blank values than gas bags, resulting in a higher percentage of quantifiable data points. The VOST method was less cumbersome and less prone to contamination than gas bags.

9. Hazardous waste samples contain a complex matrix of compounds which present a variety of analytical difficulties. Analysis by a gas chromatograph/mass spectrometer (GC/MS) was highly successful for identifying Appendix VIII compounds in the waste streams and effluents. Prescreening by a gas chromatograph/flame ionization detector (GC/FID) was useful when analyzing waste streams.

10. Because small concentrations of organics must be measured, sample contamination can present significant problems. Careful control of blanks and well defined blank correction procedures are required.

11. The results of the external and internal quality assurance program indicate that established quality assurance procedures were followed and the overall quality of laboratory and field work was adequate to meet the objectives of the study.

12. Evaluation of the QA/QC data for the eight incinerator tests indicated low or erratic recoveries in the analyses of phenol, cis- and trans-1,2-dichlorobutene, naphthalene, aniline, and bis(2-ethylhexyl)phthalate for the complex matrices encountered during this program. Caution should be used when evaluating these compounds as POHCs during actual trial burns. Further evaluation of analytical methods for these compounds is recommended.

13. The results from waste sampling and analysis at plants where Appendix VIII compounds were spiked into the liquid waste feed line indicate that inadequate mixing and, as a result, nonrepresentative samples may

be a problem at some facilities. One approach to alleviate the problem is the use of in-line mixers. This approach was successful at the one facility where it was used during the program.

2.2 RECOMMENDATIONS

1. The data collected from the eight incinerator tests showed a strong correlation between concentration of an Appendix VIII compound in the waste feed and the DRE for that compound. These data or relevant combustion theory are not sufficient to conclusively identify mechanisms which might cause such a relationship. Further parametric studies that provide a better understanding of the relationship between POHC waste feed concentrations and DRE using either pilot-scale or full-scale facilities are recommended.

2. Since data generated on this program did not fully characterize the effects of temperature, residence time, O_2 content in the stack gas, and heat input on DRE or the potential mechanisms of PIC formation, additional pilot-scale and full-scale studies to further examine these phenomena are recommended.

3. Compliance with the particulate standard was a problem for five of the eight incinerators tested. Further, the particulate emissions at five sites tested for metals contained some level of Appendix VIII metals that entered the incinerator in the waste feed. However, the data were not sufficient to define specific metals emission rates or control levels. Further studies on the generation and control of particulate emissions, and specifically metals emissions, are recommended.

4. Since the concentrations of CO and THC do not always provide good prediction of incinerator DRE, further studies to examine possible continuous monitoring techniques that do predict incinerator DREs are recommended.

5. The VOST method that was developed and used during this study appeared to provide good results for most volatile compounds in the stack gas. However, the activities of this study were not adequate for methods validation. A complete study to validate the VOST method for sampling volatile organic compounds in incinerator stack gases is recommended.

6. Because confirmation of incinerator performance demands accurate measurement of low concentrations of organic compounds in incinerator stack gases, sample contamination and the attendant blank correction methods can be a problem. A blank correction method based on methods described in the literature was used during this program. However, a well-defined, consistent procedure for blank correction on future incinerator tests should be developed and validated.

7. Since no standard procedures have been defined for data handling and reduction, significant resources were expended in developing and implementing procedures during this program. Development of well-defined standard procedures for data handling and reduction is recommended in order to expedite trial burn data handling and insure high quality and consistent data from future trial burns.

SECTION 3.0

PROGRAM DESCRIPTION

This complex program encompassed a wide array of activities from methods evaluation, to sampling and analysis, to data evaluation, and generated a large volume of information and data. This section presents the objectives and basic approach to the program, provides background descriptions of the sites where data were gathered, and summarizes data evaluation efforts. The following specific subsections present program objectives, program approach, site selection and characteristics, brief process descriptions, a summary of sampling and analysis activities and a description of data evaluation efforts.

3.1 PROJECT OBJECTIVES

The primary objective of the program was to gather the data necessary for EPA to describe the current baseline performance of hazardous waste incinerators in the United States. The data were gathered as input to the Environmental Protection Agency's regulatory impact analysis for hazardous waste incinerators. The primary measures of performance of the incinerator were destruction and removal efficiency for hazardous organic constituents, particulate emissions, and hydrogen chloride emissions. A second objective was to gather data and evaluate these data to increase knowledge of relationships between parameters that affect the performance of hazardous waste incinerators. The program did not include designed experiments to quantify relationships, but rather embodied overview assessments of the importance of various parameters.

3.2 PROGRAM APPROACH

The program was not amenable to preparation of an initial, detailed technical approach because new, developmental sampling and analysis methods were required, the urgency of the data gathering prevented identification of all sites before sampling started at the first site, and each site entailed unique measurement needs.

Initially, an array of types of measurement potentially needed to characterize sites and evaluate performance was identified and applicable sampling and analysis methods were reviewed. Methods were selected, where methods were available, to provide quality data with desired detection limits. Review and consultation with EPA led to identification of the need for a better, more sensitive method to collect samples of volatile organic compounds in incinerator stack gases. A concept for a volatile organic sampling train (VOST) was developed at a meeting with EPA, and a laboratory study was planned to evaluate the concept. A short laboratory evaluation was then conducted using a simulated gas stream (see Appendix A).

While the laboratory evaluation was underway, general preparations were initiated to conduct a series of field tests. QA/QC planning was conducted and example sampling and analysis (S&A) matrices were developed to aid decisions on the specific measurements at the first site. Standard operating procedures were developed as needed to supplement existing procedures. S&A supplies were obtained, and a system was designed and built to allow spiking of POHCs into waste feed lines. Immediately after the laboratory evaluation, VOSTs were constructed suitable for field use.

The test sites were selected by EPA to provide a broad representation of hazardous waste incinerators in the country. Incinerator type and operating parameters as well as the physical properties and chemical compositions of the waste burned were considered. The selections were constrained by the suitability of sites for testing and the ability to obtain quick access to the sites. Characteristics of the sites selected are described in Section 3.3 and process descriptions are presented in Section 3.4.

As each test site was selected, a series of activities was initiated that culminated in a summary report of the results for each site. Initial activities included preparation of a site specific test plan, general arrangements and coordination with the site, and a pretest survey. The test plans included specification of all samples to be collected, the S&A methods to be used, and process data collection. Each plan was unique due to differences in site configurations, sample collection constraints, and EPA's specific data needs; however, some elements of the plans were common to all or most sites.

As a minimum at each site, sufficient S&A was conducted to determine DREs for the major Appendix VIII compounds burned, stack emissions of Appendix VIII compounds, particulate emissions and chloride emissions. The detection limit goal for Appendix VIII compounds was to quantify a DRE of 99.999% when the waste concentration is 100 ppm or higher. At most sites carbon tetrachloride and trichlorethylene were spiked into the waste, if not already present, to provide a set of data for these two compounds across sites. These data facilitated later data analysis. A summary of the S&A for each site is presented in Section 3.5.

After the initial activities were completed, the site specific test plan was finalized. The field test was conducted and the specified samples were collected and returned to the analytical laboratory for analysis. Full QA/QC was included in the S&A, including laboratory audits for all sites and field audits at three of the eight sites. As soon as the analytical results were available, all necessary calculations (DRE, blank corrections, etc.) were made and summary test reports were prepared. All of the summary test reports are contained in Appendices C through J.

Data from the eight tests were then used in the data analysis phase of the program. Particular emphasis was placed on evaluating the quality of the data and searching for variables that affected DRE. The data analysis covered three areas; 1) data reduction and assessment of data quality, 2) evaluations of specific issues, and 3) general identification of trends or relationships in the data. A variety of statistical and engineering analysis techniques were used, with the selected techniques matched to the quantity and type of data available to address each question. The data analysis activities are summarized in Section 3.6.

The final phase of the program was to document all S&A results and methods and prepare the final report.

3.3 OVERVIEW OF SITE CHARACTERISTICS

EPA selected eight hazardous waste incinerator facilities as discussed in Section 3.2. These eight facilities were:

Ross Incineration Services, Inc. - Grafton, Ohio
Plant B
Upjohn Company - LaPorte, Texas
Zapata Industries, Inc. - Butner, North Carolina
American Cyanamid - Willow Island, West Virginia
Mitchell Systems, Inc. - Spruce Pine, North Carolina
Du Pont Pontchartrain Works - LaPlace, Louisiana
Trade Waste Incineration, Inc. - Sauget, Illinois

The facilities represent a wide range of key incinerator design and operating parameters and waste feed characteristics. Some of the more important characteristics include incinerator type; incinerator operating parameters such as combustion temperature, residence time, heat input rate, and excess air; type and operating characteristics of particulate and HCl control equipment; and waste characteristics such as physical state, organic content, moisture content, heating value, and ash and chloride content.

An overview of the range of characteristics exhibited by these eight sites is presented in Table 3-1. Process descriptions for each site are presented in Section 3.4 with further detail in Appendices C-J.

The distribution of incinerator types and control devices is shown in Table 3.1 Each of the eight incinerators had liquid injection burners; four of those fired both organic and aqueous wastes during the tests. Three of the facilities fired solid wastes (two rotary kilns and one hearth) and one ducted gaseous waste to the incinerator during testing. Three incinerators had no air pollution control devices, and the other five had scrubbers for HCl control. Particulate control at four plants included an electrified wet scrubber and two venturi scrubbers.

The facilities also can be classified as on-site and off-site, with four in each class. On-site facilities are located at the waste generation site and dispose of wastes from a single firm or process. Off-site facilities are commercial disposers that handle wastes from a large number of sources. Off-site facilities generally have larger capacities.

TABLE 3-1. DISTRIBUTION OF INCINERATOR TYPES AND CONTROL DEVICES

Incinerator type	Number of facilities
Liquid injection	8
Rotary kiln	2
Hearth	2
Gas injection	1
Control device	Number of facilities
None	3
HCl scrubber	5
Particulate control	4

On-site facilities ranged in capacity from 50 to 1,400 kg/hr (100 to 3,000 lb/hr) of waste feed or 1 to 33 GJ/hr (1 to 31 million Btu/hr) heat input, while off-site facilities ranged from 600 to 6,000 kg/hr (1,300 to 13,000 lb/hr) of waste feed or 9 to 78 GJ/hr (9 to 74 million Btu/hr) heat input. Off-site facilities generally incinerated a much greater variety of wastes. Solid and aqueous liquid wastes were more frequently handled at off-site facilities, and both the physical state and chemical composition of the wastes were much more varied than at on-site facilities.

Values for design and operating parameters also varied widely from facility to facility. Each facility had unique design or operating features. Multiple combustion chambers were common, some with separate waste feeds. Example arrangements of multiple chambers were parallel chambers (e.g., a kiln for solid wastes and a separate liquid injection unit) or primary and secondary chambers in series.

Wide ranges were exhibited for three key parameters: combustion temperature, residence time, and percent excess air or percent oxygen. Operating temperatures ranged from 820° to 1100°C (1500° to 2100°F). The values presented are those recorded on each facility's instruments. They represent a fair picture of the range of values; however, when comparing values from site to site the location of the thermocouple is important. The temperature reading can vary a few hundred degrees depending on the thermocouple location. Calculated residence times varied from 0.07 to 6.5 sec. Again, the range is representative, but individual values are difficult to interpret. Values were calculated from combustion chamber volumes and average flow rates. At times a section of the stack or duct contained gases at high temperature and might legitimately be considered part of the combustion volume. At facilities with multiple chambers at different temperatures, selection of the proper time/temperature is difficult. Excess air values fell within a range of 60 to 130%. Corresponding oxygen content ranged from 8 to 12%.

Operating conditions during the tests were those selected by the plants as their normal conditions. In general, any existing operating problems were corrected before the tests were initiated.

The wastes fired at the different facilities varied with respect to waste type, heating value, chloride, ash, and moisture content. Two of the eight facilities handled only organic liquid waste; two handled organic and aqueous liquid waste; two handled organic and aqueous liquids and solid wastes; one handled liquid and gaseous organic wastes, and one handled direct injection liquid organics and drummed liquid organic and solid wastes.

Figure 3-1 shows the variation in some waste characteristics by type of waste. The heating values were below 4,600 kJ/kg (2,000 Btu/lb) for aqueous liquids and ranged from 14,000 to 37,000 kJ/kg (6,000 to 16,000 Btu/lb) for organic liquids, and from 0 to 29,000 kJ/kg (0 to 12,500 Btu/lb) for solid wastes. The organic liquids and many of the solids had a high enough heating value to sustain combustion without auxiliary fuel. Percent chloride in the wastes ranged up to 25%, with the highest values occurring for organic liquids (chlorinated solvents). Little ash was found in aqueous liquids, values for organic liquids ranged up to 9%, and solids had the most ash with values from 17% to 29%. Water content is obviously high for the aqueous wastes, but ranged up to 50 to 60% for the organic liquids and solids.

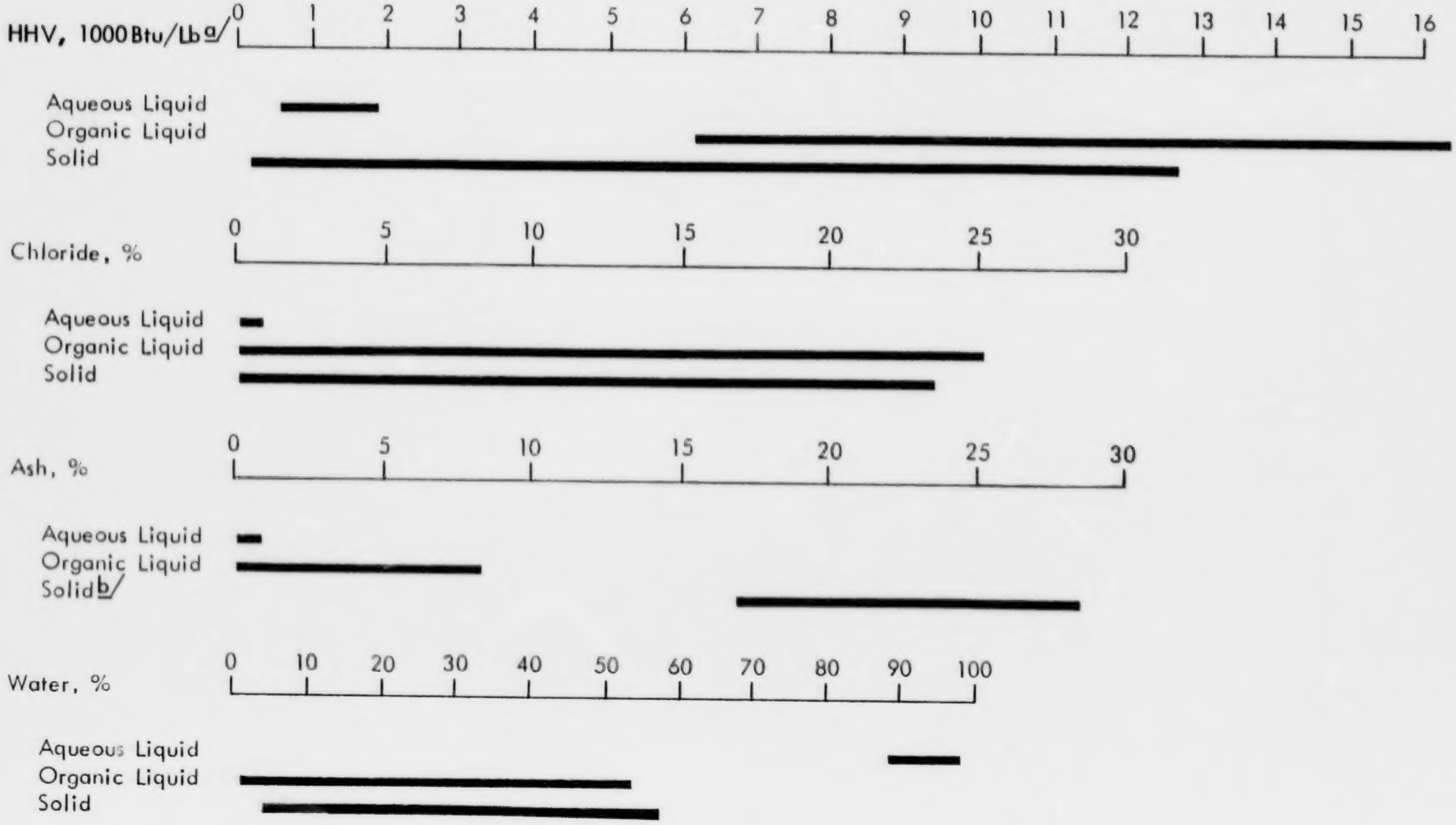
3.4 PROCESS DESCRIPTIONS

Each of the eight facilities tested has unique design and process characteristics. The subsections below describe the design and operations of each facility, and summarize key process and waste feed characteristics.

3.4.1 Site Descriptions

The paragraphs below provide brief descriptions of seven of the facilities (except Plant B). More detailed descriptions are provided in Appendices C-J.

As shown in Figure 3-2a, the Ross incinerator comprises two chambers in series, a rotary kiln and a large nearly rectangular combustion chamber. The four waste feed streams handled by this off-site facility are: (a) an aqueous waste that is fed to the combustion chamber; (b) an organic liquid waste fired into the combustion chamber; (c) drummed solid wastes that are fed to the kiln; and (d) drums of solid waste on metal "sleds" that are placed directly in the combustion chamber through a side door. The process uses two packed bed caustic scrubbers in series for HCl control and an electrified scrubber for particulate control.



a/ 1,000 Btu/Lb = 2,300 kJ/kg

b/ Does not include sand spiked with chlordane at TWI

Figure 3-1. Waste characterization.

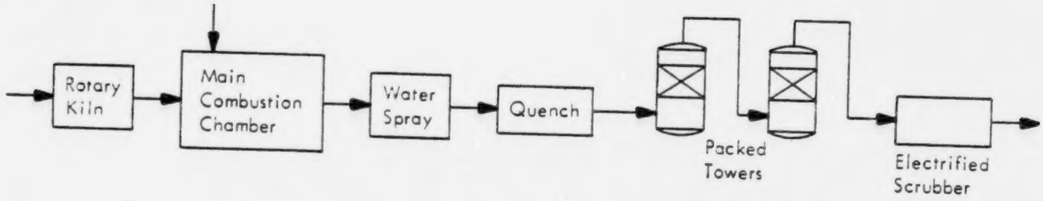

Rotary Kiln
Main Combustion Chamber
Water Spray
Quench
Packed Towers
Electrified Scrubber

Figure 3-2a. Schematic of the Ross System.

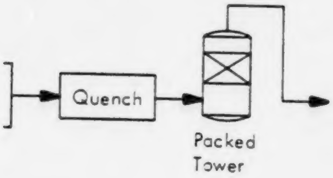

Quench
Packed Tower

Figure 3-2b. Schematic of the Upjohn System.

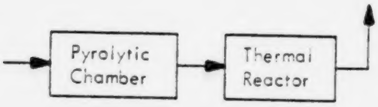

Pyrolytic Chamber
Thermal Reactor

Figure 3-2c. Schematic of the Zapata System.

The Upjohn incinerator is an on-site facility at a chemical plant that is designed to burn liquid and gaseous production waste. The incineration system, shown in Figure 3-2b, consists of a small burner/ignition chamber followed by a horizontal cylindrical thermal oxidizer chamber. The liquid waste, natural gas and combustion/atomizing air are fed to the burner assembly, and the waste gas is vented directly to the ignition chamber. The facility uses a single pass counter-current packed bed scrubber with water only to control HCl emissions. Upjohn has no particulate control device.

The Zapata industries incineration facility shown in Figure 3-2c is an on-site incinerator designed to burn varnish and lacquer wastes from an industrial process. The incinerator has two chambers, a pyrolytic chamber and a thermal reactor. The waste is fed to the pyrolysis chamber from a waste feed tank. The system has no control equipment for particulates or HCl.

The American Cyanamid incinerator is an on-site facility designed to burn waste streams from chemical processes. As shown in Figure 3-2d, the incinerator has two chambers. Waste and primary air enter a small mixing chamber and pass to the combustion chamber where secondary air is added. Two different liquid organic waste streams--an aniline waste and a mononitrobenzene waste--are burned separately at the facility. The system has no control equipment for particulate or HCl removal.

The Mitchell Systems Inc. incinerator shown in Figure 3-2e is an off-site facility designed to burn principally liquid wastes but capable of handling small quantities of solid wastes. During the tests only liquid wastes were burned. Two liquid waste streams, one liquid organics and the other an aqueous waste, are fed to the primary combustion chamber through air-atomized injectors. The facility has no equipment for particulate or HCl control.

The Du Pont facility is an on-site incinerator at a chemical plant, but also handles wastes from other Du Pont plants. As shown in Figure 3-2f, the system has two parallel incinerators discharging through a common scrubbing system. One of the parallel components is a rotary kiln incinerator with a natural gas fired afterburner, and the other component is a single stage liquid injection incinerator. The rotary kiln incinerator burns five different waste streams--two different coke wastes, a filter cake waste, waste paint, all of which are fed in barrels intermittently, and a continuous feed of liquid organic waste. The liquid injector burns only a liquid organic waste stream. Both systems feed into venturi scrubbers followed by cyclonic separators for particulate control. The common control system has three absorber scrubbers (one disk and donut and two packed towers) in series for HCl control.

The TWI incinerator is a commercial off-site facility that burns liquid and solid wastes. As shown in Figure 3-2g, the facility has a two stage combustion system. Two liquid waste streams, a liquid organic stream and an aqueous waste stream, are fed to the primary chamber through separate lines. Solid waste is fed to the primary chamber by ram injection. Fuel oil and combustion air are fed to both the primary and secondary chambers for temperature control. A Venturi scrubber with a cyclonic separator and two-stage mist eliminator is used for particulate and HCl control.

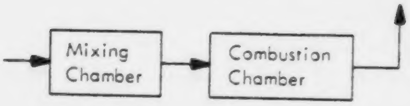

Mixing Chamber
Combustion Chamber

Figure 3-2d. Schematic of the American Cyanamid System.

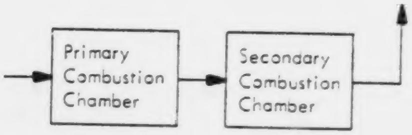

Primary Combustion Chamber
Secondary Combustion Chamber

Figure 3-2e. Schematic of the Mitchell System.

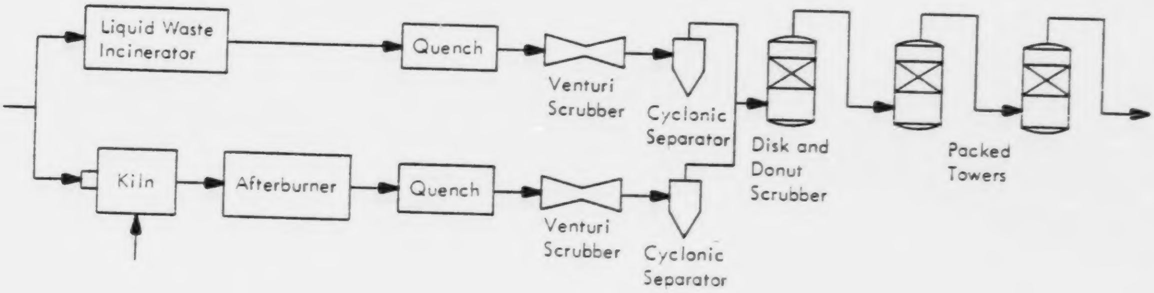

Liquid Waste Incinerator
Quench
Venturi Scrubber
Cyclonic Separator
Disk and Donut Scrubber
Packed Towers
Kiln
Afterburner
Quench
Venturi Scrubber
Cyclonic Separator

Figure 3-2f. Schematic of the Du Pont System.

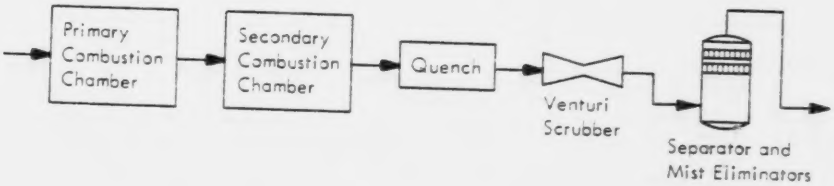

Primary Combustion Chamber
Secondary Combustion Chamber
Quench
Venturi Scrubber
Separator and Mist Eliminators

Figure 3-2g. Schematic of the TWI System.

3.4.2 Process and Waste Feed Characteristics

The performance of a hazardous waste incinerator with respect to POHC destruction, particulate emissions and HCl emissions, may be affected by a number of incinerator operating parameters and a variety of waste feed characteristics. This section summarizes some of the key process and waste characteristic data for each of the eight facilities tested. More comprehensive presentations of the data are contained in Appendices C-J.

Key process parameters that previously were identified as important to incinerator performance are combustion temperature, residence time, excess combustion air (or excess oxygen) and total heat input. These parameters were quantified to the degree possible during each of the eight tests. Table 3-2 presents these data for each run at seven of the eight facilities. As discussed in Section 4.3.3, quantification of the parameters was difficult, and the values presented in the tables should be used with caution.

Key waste feed parameters that impact incinerator performance include POHC identity and concentration, heating value, ash content, chloride content and moisture content. The POHC data for the eight facilities are tabulated in Appendices C-J. The other data are tabulated on a by run basis in Table 3-3.

3.5 SAMPLING AND ANALYSIS PROCEDURES

Sample locations and sampling and analysis (S&A) procedures were unique for each facility tested, because of differences in system designs, operating practices, and waste characteristics. Appendices C-J identify the specific sample locations, sample procedures, and analytical methods that were associated with each facility. Descriptions of the methods and procedures are provided in Appendix B.

While specific S&A plans were unique for each test facility, the overall approach was common for all sites. The objective of this approach was to characterize all the incinerator input and output streams to the greatest degree possible. Input streams generally included waste feeds, auxiliary fuel, and control system makeup waters. Output streams generally included stack gases, control device effluent, and incinerator bottom ash. Table 3-4 presents an overview of the S&A activities at the eight facilities. A brief overview of the methods identified in Table 3-4 is presented below.

The method of sampling effluents consisted of grap sampling for waste feeds, ash, and makeup and effluent waters, and solids from air pollution control equipment. Stack sampling was accomplished using a Modified Method 5 (MM5) train for particulates, chlorides, metals, and semivolatile POHCs. Two methods were used for sampling volatile POHCs; gas bags, and VOST. Continuous monitors were used for O_2, CO_2, CO, and total hydrocarbons. Since the grab sampling techniques were unique for each stream, descriptions are deferred to Appendix B. Brief descriptions of the stack sampling and analysis methods are presented below.

TABLE 3-2. SUMMARY OF KEY PROCESS PARAMETERS

Facility	Run No.	Temperature °C	Residence/time sec	Heat input 10^6 kJ/hr	Excess oxygen % O_2 in stack
Ross	1	1154	6.2	87	10.4
	2	1146	6.5	60	10.5
	3	1117	6.7	87	10.7
Upjohn	2	1116	5.2	6.2	8.1
	3	1116	5.2	6.3	8.3
	4	1116	5.2	6.1	8.4
Zapata	1	671/854[a]	0.069	1.5/1.9[b]	8.2
	2	721/868	0.067	1.7/2.1	12.0
	3	738/845	0.066	1.0/1.5	11.8
	4	690/905	0.063	0.70/1.0	11.9
American Cyanamid	1	779[c]	0.17	5.0	10.3
	2	671	0.21	5.0	12.4
	3	629	0.24	4.4	No Data
	4	679	0.23	4.7	12.7
	5	648	0.21	4.5	13.1
Mitchell	1	1052/1010[d]	2.5	8.3	9.4
	2	1065/1093	2.4	9.0	9.5
	3	1093/1121	2.2	10.5	No Data
	4	1079/1079	2.2	6.2	10.3
DuPont	1	807/1000/1450[e]	7.2/0.26[f]	19/17[g]	9.2
	2	750/975/1450	7.0/0.25	17/17	9.6
	3	750/967/1450	7.6/0.28	19/17	10.3
TWI	1	1137/1110[h]	4.7	7.7	12.4
	2	1110/1093	3.5	7.9	13.0
	3	1132/1110	3.5	6.3	13.2
	4	988/966	3.0	7.4	15.6

[a] First value is main chamber temperature, second value is secondary chamber temperature.

[b] First value represents only waste heat input, second value includes natural gas heat input.

[c] Temperature measured in stack near entrance.

[d] First value is upper chamber temperature, second value is lower chamber temperature.

[e] First value is kiln temperature, second temperature is afterburner temperature, third value is liquid injector temperature.

[f] First value is the kiln/afterburner residence time, the second value is the liquid injector residence time.

[g] First value is kiln heat input, second value is liquid injector heat input.

[h] First value is primary chamber temperature, second value is secondary chamber temperature.

TABLE 3-3. SUMMARY OF WASTE FEED CHARACTERISTICS

Plant	Waste stream	Run no.	Heating value (kJ/kg)	Ash %	Chlorides %	Moisture %
Ross	Drum waste to kiln	1	18,680	36.9	0.019	27
		2	21,810	40.0	1.6	19
		3	22,100	41.0	0.12	14
	Drum waste to chamber	1	23,750	0.55	7.6	2.3
		2	19,010	0.51	7.5	8.4
		3	23,830	0.25	6.7	7.3
	Aqueous waste	1	1,570	0.25	0.04	98
		2	1,560	0.25	0.04	94
		3	1,510	0.26	0.03	95
	Liquid organic	1	21,890	2.42	6.2	24
		2	20,150	2.12	5.6	21
		3	22,230	2.28	5.4	23
Plant B	Liquid organic	1	19,760	4.9	5.4	35
		2	20,400	4.8	6.6	38
		3	19,710	4.7	5.4	48
	Aqueous	1	4,090	1.2	0.50	94
		2	4,480	1.1	0.57	95
		3	4,520	1.0	0.41	97
Upjohn	Liquid	2	23,770	0.17	21	[a]
		3	23,500	0.19	22	[a]
		4	23,980	0.21	21	[a]
	Gaseous	2	8,200[b]	0	132[c]	0
		3	8,200[b]	0	168[c]	0
		4	8,200[b]	0	239[c]	0
Zapata	Liquid organic	1	37,540	0.018	2.7	0.68
		2	37,890	0.013	1.6	0.63
		3	22,800	0.0098	1.3	37
		4	15,230	0.14	0.74	54
American Cyanamid	Aniline waste	1	33,700	0.16	0.018	6.0
		2	33,750	0.19	0.015	5.2
		3	33,670	0.19	0.020	5.5
		5	33,620	0.50	0.019	7.3
	Mononitrobenzene waste	4	25,060	< 0.05	0.013	0.57

(continued)

TABLE 3-3. (continued)

Plant	Waste stream	Run no.	Heating value (kJ/kg)	Ash %	Chlorides %	Moisture %
Mitchell	Aqueous	1	1,810	0.70	0.39	89
		2	1,700	0.78	0.36	94
		3	1,530	0.74	0.26	90
		4	1,600	0.80	0.38	90
	Organic	1	34,120	1.5	1.0	2.2
		2	34,400	2.1	1.3	3.2
		3	37,090	2.4	0.72	5.7
		4	34,650	0.78	1.2	2.4
DuPont	Liquid organic	1	29,110	0.47	25	2.8
		2	28,900	0.22	25	1.8
		3	28,910	0.30	26	2.9
	Filter coke	1	8,740	17	8.3	55
		2	8,430	17	9.8	51
		3	7,990	18	9.2	56
	DCB coke	1	28,710	0.55	22	0.47
		2	28,090	0.21	25	2.7
		3	27,560	0.72	21	4.8
	ISOM cake	1	15,930	0.68	18	39
		2	14,560	1.5	17	38
		3	19,030	1.6	19	32
	Paint waste	1	32,380	1.4	0.050	0.59
		2	31,830	2.3	0.18	0.43
		3	30,720	8.2	0.14	0.51
TWI	Liquid organic	1	35,060	3.1	1.7	4.9
		2	34,700	3.5	1.7	4.7
		3	34,150	3.9	1.8	5.3
		4	32,170	4.0	4.9	5.6
	Aqueous	1	158	< 0.05	0.0097	94
		2	1,220	< 0.05	0.013	94
		3	1,920	< 0.05	0.0096	96
		4	1,920	< 0.05	0.013	95
	Solids	1	810	90	2.0	1.5
		2	790	90	2.6	1.4
		3	670	90	2.0	1.6
		4	20,040	29	5.2	11

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[a] Moisture analyses were not conducted. The moisture content is expected to be near zero because TDI was present in the waste in high concentrations, and TDI is highly reactive with water.

[b] kJ/dscm.

[c] mg/dscm.

TABLE 3-4. OVERVIEW OF SAMPLING AND ANALYSES ACTIVITIES

Stream	Sampling method/technique	Analyses	Facility							
			Ross	Plant B	Upjohn	Zapata	Cyanamid	Mitchell	Du Pont	TWI
Liquid feed	Grab	HHV	X	X	X	X	X	X	X	X
		POHC	X	X	X	X	X	X	X	X
		Cl^-	X	X	X	X	X	X	X	X
		H_2O	X	X		X	X	X	X	X
		Ash	X	X	X	X	X	X	X	X
		Metals	X	X			X	X	X	X
		Viscosity						X		X
Solid feed	Grab	HHV	X						X	X
		POHC	X						X	X
		Cl^-	X						X	X
		H_2O	X						X	X
		Ash	X						X	X
		Metals	X						X	X
Gaseous Feed	Grab/Flash Grab/Syringe Grab/Glass Cylinder	Cl^-			X					
		$COCl_2$			X					
		POHCs			X					
Control device makeup water	Grab	Chloroform		X						
		Cl^-	X	X	X				X	
		POHCs	X	X					X	X
		pH							X	
Control device effluent	Grab	pH	X	X					X	X
		POHC	X	X					X	X
		Cl^-	X	X	X				X	
		Metals	X							
Ash	Grab	POHC	X	X				X		X
		Cl^-		X				X		
		Metals		X						X
		EP toxicity		X						X
Stack	MM5	Particulate	X	X	X	X	X	X	X	X
		Metals	X	X					X	X
		Semivolatile POHC	X	X	X		X	X	X	X
		Semivolatile PIC	X	X	X		X	X	X	X
		Cl^-	X	X	X	X	X	X	X	X
	VOST	Volatile POHC	X	X	X	X	X	X	X	X
		Volatile PIC	X	X	X	X	X	X	X	X
	Gas bag	Volatile POHC	X	X	X	X	X	X	X	X
		Volatile PIC	X	X	X	X	X	X	X	X
	Gas bag	Orsat CO_2	X	X	X	X	X	X	X	X
		O_2	X	X	X	X	X	X	X	X
	Continuous monitors	CO	X	X	X	X	X	X	X	X
		CO_2	X	X	X	X	X	X	X	X
		O_2	X	X	X	X	X	X	X	X
		THC	X	X	X	X	X	X	X	X
	Special impinger train	$COCl_2$			X					
		Isocyanates			X					

X - Indicates that the sampling and analysis activity was conducted at the facility.

Gas bag samples were collected in 15-L Tedlar bags, drawing gas into the bags over a period of about 1 hr. Gas bags filled with prepure N_2 in the field were also prepared as gas bag blanks.

In addition to gas bags, two VOST sampling systems were also used to sample volatile POHCs. The VOST system consists of a Tenax trap and a backup Tenax/charcoal trap. For fast VOST, gas was drawn through the two traps, in series, at a rate of 1 L/min for 20 min. The first pair of traps was then removed and replaced with another pair, until a total of six pairs were collected (i.e., 120 min of sampling time). Slow VOST was used in addition to fast VOST at some sites. Slow VOST was similar to fast VOST, but the sampling rate was slower (0.25 L/min). The sampling time was either 20 min or 40 min, depending on the test. Field blank sample pairs were exposed to the sampling location for the same period required to insert sample traps into the VOST apparatus. The traps were then returned to the analytical laboratory for analysis of volatile POHCs.

POHCs in the waste feed and stack samples were determined by GC/MS. Prior to analysis, the waste feed samples were homogenized either manually or mechanically. The homogenized feed samples were analyzed for volatile POHCs using a protocol based on Method A101b in the A. D. Little report, "Sampling and Analysis Methods for Hazardous Waste Incineration."[1] The semivolatile POHCs were analyzed in the waste feed samples using a GC/FID screen followed by GC/MS. The protocol was based on Method P023 in the A. D. Little report.[1]

The volatile POHCs from the stack gas samples were contained in Tedlar gas bags and on the Tenax and Tenax/charcoal traps used with VOST. A known amount of the gas bag sample, usually 5.0 L, was transferred onto a Tenax/charcoal trap (the same type of trap used as the backup trap in the VOST). To make the transfer a needle was inserted into the bag and the contents drawn onto the trap at a rate of 500 mL/min for 10 min. These traps were then analyzed using the same techniques that are described below for the VOST traps.

Prior to GC/MS analysis, all Tenax and Tenax/charcoal adsorbent trap samples, transferred bag samples, and calibration standards were spiked with 50 ng of perfluorobenzene, D_4-1,2-dichloroethane, and bromofluorobenzene internal standards using the flash vaporization technique, in which the spiking solution was vaporized and carried onto the trap with a carrier gas. In order to accomplish this spiking, the glass traps were attached to the injection port (160°C) of a GC column. Helium flow, set to about 50 mL/min, was turned on through the trap and a syringe needle injected through the GC septum port. Slowly, 1 µL of a 25-ng/µL methanolic solution of the internal standards was expelled from the syringe over about a 15-sec period. At the end of about 25 sec, the gas flow through the trap was shut off and the syringe removed. The total flow of gas through the traps during spiking was only about 25 mL.

To analyze the traps, the contents of the wet traps (dry traps in the case of method blanks, field blanks, calibration standards, and gas bag samples) were thermally desorbed using a stream of carrier gas into a water column (1 to 5 mL), which is a component of the EPA Method 624 purge-trap-desorb GC/MS analysis system. The traps were desorbed at a flow rate of 100 mL/min for 10 min at 180°C. The desorbed compounds passed into the bottom of the water column, were purged from the water, and then were collected on an analytical adsorbent trap also containing Tenax and charcoal. The compounds were then desorbed from the analytical adsorbent trap into the GC/MS system per EPA Method 624.

Analysis of semivolatile POHCs in the stack involved several components of the MM5 train. Each of the components of the MM5 train was spiked with a separate surrogate standard according to the following scheme:

Front XAD-2 resin trap - 20 μg of ^{13}C-tetrachlorobiphenyl

Back XAD-2 resin trap - 20 μg decafluorobiphenyl

Particulate filter plus probe rinse residue - 20 μg of D_{12}-chrysene

Condensate water - 20 μg of D_8-naphthalene

The spiked components were normally extracted separately and the extracts combined, dried with anhydrous sodium sulfate, concentrated to 1.0 mL using Kuderna-Danish evaporation according to Method P031 in the A. D. Little report[1] and using supplementary gentle nitrogen blowdown, and analyzed by fused silica capillary column GC/MS. The samples were extracted according to the following procedures:

XAD-2 resin traps: The XAD-2 resin traps were Soxhlet-extracted with methylene chloride for 16 hr as described in Method P024B in the A. D. Little report.[1]

Particulate filters plus probe rinse residues: The residue from the acetone rinse of the probe was added to the particulate and Soxhlet-extracted with methylene chloride for 16 hr as described in Method P024b in the A. D. Little report.[1]

Condensate water: The condensate water was extracted with three 60-mL aliquots of methylene chloride as described in Method P021a in the A. D. Little report (equivalent to EPA Method 625).[1]

POHCs in scrubber water and ash samples were analyzed using the procedures described above. To analyze for metals, the samples were acid digested and analyzed by inductively coupled argon plasma emission spectrophotometry and/or atomic absorption spectrophotometry. Particulate and chloride analyses were conducted according to EPA Method 5 and EPA Method 325.2, respectively, from "Methods for Chemical Analysis of Water and Wastes."[2] EP toxicity tests were conducted according to Federal Register, 45, May 19, 1980.[3] Water content in the waste feeds was determined by the Karl Fischer titration method. Chlorine in the waste feed and chamber ash was determined by potentiometric titration using a Fischer Titralizer Model 41. To determine bromine content, waste feed samples were combusted in a Shoniger flask, the bromine oxidized to bromate with hypochlorite, and the excess hypochlorite destroyed upon acidification with sulfuric acid. Potassium iodide was then added and the liberated iodine was titrated with thiosulfate. Heating value was determined by ASTM Methods D2015-66[4] and D240-64.[5] Orsat analyses were performed according to EPA Method 3. Continuous monitoring involved the following:

O_2 - Beckman Model 742 (polarographic sensor)

CO - Beckman Model 215A (nondispersive infrared)

HC - Beckman Model 402 (heated oven flame ionization detector)

CO_2 - Horiba Model PIR-2000S (nondispersive infrared)

3.6 DATA EVALUATION ACTIVITIES

The S&A activities described in Section 3.5 generated a very large number of data points of potential use to evaluate incinerator performance. The objectives of the data evaluation phase of the study were: (a) to reduce the data to a format that is most useful for evaluating incinerator performance; (b) to define those incinerator and waste parameters that have the greatest impact on incinerator performance; (c) to evaluate the magnitude of those impacts to the degree possible within the available data base and (d) to assess the overall quality of the data generated during a trial burn. To accomplish these objectives the data evaluation was divided into three distinct concurrent activities: (a) data reduction and calculations; (b) specific issue analyses; and (c) pattern recognition activities. Each of these data analysis activities is described briefly in the paragraphs below.

The initial data evaluation activity was the development of procedures to reduce data to a format most useable for subsequent analyses. Activities under this segment include evaluating and defining procedures for calculating chloride and POHC input rates, blank correction procedures for POHC effluent rates, and calculation of the most reasonable residence time and excess air for each of the eight facilities. A significant problem addressed during this component was the methodology for correcting stack POHC and PIC effluent rates for blank values. This problem is related to the relatively small concentrations in the stack in comparison to plant and laboratory ambient levels of organic hazardous constituents. Potential trap and sample contamination can make determination of appropriate blank levels difficult. The findings related to blank correction and procedural recommendations are presented in Section 4.3.

A number of specific technical issues related to incinerator performance were identified throughout the program. Specific engineering and statistical analysis techniques appropriate to each problem were selected and, to the degree possible within the available data base, conclusions were drawn. Table 3-5 identifies the major specific issues addressed during the program and the analytical techniques used. One specific issue of note is the detailed review of available QA/QC data to assess the potential quality of the trial burn data. Basic descriptive statistics were developed

TABLE 3-5. SUMMARY OF SPECIFIC DATA EVALUATION ACTIVITIES

Issues	Analytical Techniques
Assessment of overall data quality	Multiple techniques including calculation of descriptive statistics related to accuracy and precision, and chemical and engineering analyses of potential problems and causes
Relationship between DRE and heats of combustion	Nonparametric rank order correlation
Relationship between DRE and waste feed concentration	Linear regression on log transforms, and Engineering analysis of potential reaction rates
PIC formation	Chemical and engineering analyses of potential formation mechanisms Graphical comparison of PICs and POHCs
Potential for Dioxin/Furan formation	Review of Dixoin/Furan formation and presence of precursors in waste
Relationship of CO/THC concentrations to POHC stack concentration and DRE	Nonparametric statistics - rank order correlation and distribution free rank sum test
Performance of air pollution control equipment	Comparison of data between systems and engineering analysis of system performance
Achievability of 99.99% DRE	Multiple techniques including comparison of basic descriptive statistics, linear regression analyses, and discriminant analyses

for all tests, and potential problem areas were examined. The results of these analyses are presented in Sections 4.1 and 4.2.

The objective of the pattern recognition component of the data evaluation effort was to identify relationships between parameters that were not apparent from the overall examination of the data. To achieve this objective the pattern recognition approach employs a variety of multivariate statistical techniques. The two techniques that were most productive on this program were factor analyses which identified the parameters that contributed most significantly to the overall variation in the test data and discriminant analyses which were used to identify the incinerator and waste characteristics that contributed most significantly to the achievement or nonachievement of 99.99% DRE. The results from these analyses are presented in Section 4.1.

3.7 REFERENCES

1. Harris, J., D. Larsen, C. Rechsteiner, and K. Thurn, "Sampling and Analysis Methods for Hazardous Waste Combustion, First Edition," prepared for U.S. Environmental Protection Agency, Contract No. 68-02-3211 (124) by Arthur D. Little, Inc., February 1983.

2. "Methods for Chemical Analysis of Water and Wastes," EPA-600/4-79-020, U.S. Environmental Protection Agency, March 1979.

3. Federal Register, 45 (98), Monday May 19, 1980, pp. 33127-33128.

4. "Annual ASTM Standards, Vol. 26, Gaseous Fuels, Coal and Coke; Atmospheric Analysis," American Society for Testing and Materials, 1974, pp. 468-475.

5. "Annual ASTM Standards, Vol. 23, Petroleum Products and Lubricants," American Society for Testing and Materials, 1974, pp. 149-155.

SECTION 4.0

DISCUSSION OF RESULTS

Two key questions that provided the overall focus for this program were: (a) how well can hazardous waste incinerators typically perform, and (b) what conclusions about, or insights into, the performance of an incinerator can be drawn from other trial burn results? Complex issues involving sampling and analysis procedures, incinerator design and operating characteristics, and control equipment design and performance affect the answers to these questions. While the results of this program do not provide complete answers to the two questions, they do provide information that will contribute to understanding a number of related specific issues.

This section presents the more significant results from this program. Additional information is presented in the appendices. Because the questions related to incineration are complex and not fully answered by this program, the results presented here tend to be discrete pieces of information rather than a cohesive body of knowledge that completely characterizes incinerator performance. These results are a synopsis of available information, not answers to general questions.

The results have been divided into general subject areas in the subsections below. The first subsection discusses incinerator operation and performance related to destruction and/or formation of organic hazardous constituents. The impacts of incinerator design and operating conditions and waste characteristics on organic emissions are also discussed. The second subsection discusses control of chloride and particulate emissions. The subsection presents emissions data, describes control systems and evaluates the performance of those systems for HCL, particulate, and metals emissions. The third subsection addresses the quality of results from the eight tests and draws inferences related to potential quality of trial burn results. It includes discussion of quality assurance/quality control (QA/QC) results, potential process monitoring problems, and data handling and reduction. The last subsection deals with sampling and analysis (S&A) considerations. It describes some specific S&A procedures that were developed or modified to address the peculiarities of incinerator testing and some of the specific problems that were encountered.

4.1 INCINERATOR ORGANIC EMISSIONS AND THEIR CONTROL

The most prevalent parameter used to assess incinerator performance is DRE for POHCs in the waste feed. In this section the DRE data are summarized and compared to a variety of other factors such as waste feed composition, heat of combustion, and operating conditions. Analysis aimed at explaining the presence of products of incomplete combustion (PICs) is also presented in this section. PICs are defined as hazardous organics detected in the stack gas that were either in the waste feed in low concentrations (< 100 μg/g) or not detected in the waste at all. Finally, continuous measurements for carbon monoxide (CO) and total hydrocarbons (THC) in the stack gas were analyzed to determine if any relationship existed between CO, THC, and hazardous organics in the stack effluent.

4.1.1 POHCs

Monitoring of POHCs occurred at several points throughout the incinerator operation. This section discusses the destruction and removal of POHCs and their presence in various effluents. DREs are summarized for all volatile and semivolatile compounds. The impact on DREs of waste feed concentration, heat of combustion, incinerator operating conditions and control equipment, are examined.

4.1.1.1 Summary of DREs--

All waste feed streams to the eight incinerators were analyzed for Appendix VIII compounds. For each facility, all of these compounds found at concentrations above 100 μg/g (approximate detection limit) in at least one waste stream were classified as POHCs. The most frequently encountered POHCs were toluene, tetrachloroethylene, carbon tetrachloride, and trichloroethylene. The last two were spiked into the waste feed at six of the facilities. This was done to enable some comparison among this series of tests and others being done or planned for the EPA Thermal Destruction Program.

Mass rates determined for POHCs in the waste feed streams and the stack effluent are listed in Appendices C through J. These mass rates for stack effluents were blank corrected using the procedure outlined in Section 4.3.3, and the DRE was calculated for each POHC in the waste feed using the following formula:

$$\mathrm{DRE} = \frac{W_{in} - W_{out}}{W_{in}} \times 100$$

where W_{in} - mass rate of POHC in waste feed (g/min)

W_{out} - mass rate of POHC in stack gas (g/min)

A data base was established using the fast VOST values for volatiles and the MM5 values for semivolatiles. Fast VOST was chosen because it displayed fewer blank problems than gas bags (especially in the last five tests) and provided a more complete data set than slow VOST. Tables 4-1 through 4-8 list the DREs calculated from the fast VOST and MM5. This list is considered the best available data base and was used for data analyses except when noted otherwise. For a more specific discussion of the uncertainties associated with the values in these tables, refer to the individual test reports (Appendices C through J) and the discussion of data quality (Section 4.3).

TABLE 4-1. DESTRUCTION AND REMOVAL EFFICIENCIES (DREs) FOR THE ROSS INCINERATOR - BLANK CORRECTED

Volatile compounds	Fast VOST		
	Run 1	Run 2	Run 3
Carbon tetrachloride	> 99.9964	> 99.9961	> 99.9959
Trichloroethylene	> 99.99936	99.9965	99.9969
Tetrachloroethylene	> 99.9986	> 99.9977	99.99912
Toluene	> 99.99904	> 99.9987	> 99.9978
Methylene chloride	> 99.968	> 99.989	> 99.978
Methyl ethyl ketone	99.99967	99.99930	99.99932
1,1,1-Trichloroethane	99.99952	> 99.9990	> 99.999
1,1,2-Trichloroethane	> 99.999994	> 99.999994	> 99.999994

Semivolatile compounds	MM5		
	Run 1	Run 2	Run 3
N,N-Dimethyl acetamide	> 99.9998	> 99.9999	> 99.9999
Phenol	> 99.997	> 99.993	> 99.992
2,4-Dimethyl phenol	99.9992	99.9990	> 99.9994
Naphthalene	> 99.994	> 99.994	> 99.991
Butyl benzyl phthalate	> 99.9996	> 99.998	> 99.999
Phthalic anhydride	a	> 99.99	> 99.99
Aniline	> 99.998	> 99.998	> 99.998
Methyl pyridine	> 99.998	> 99.998	> 99.998
Cresol(s)	> 99.9993	> 99.999	> 99.9991

[a] Waste feed concentration < 100 μg/g in this run.

TABLE 4-2. DESTRUCTION AND REMOVAL EFFICIENCIES (DREs) FOR THE PLANT B INCINERATOR - BLANK CORRECTED

Volatile compounds	Fast VOST[a]		
	Run 2		Run 4[b]
	Inlet	Outlet	Inlet
Chloroform	> 99.928	> 99.86	> 99.69
Carbon tetrachloride	IF	IF	IF
Trichloroethylene	> 99.993	> 99.983	> 99.949
Tetrachloroethylene	> 99.9988	> 99.9966	99.948
Toluene	> 99.9978	99.989	< 99.9940

Semivolatile compounds	MM5		
	Run 1	Run 2	Run 3
Phenol	99.979	99.989	99.976
Naphthalene	99.85	99.81	99.927
Diethyl phthalate	99.962	99.943	99.974
Butyl benzyl phthalate	99.9938	99.92	99.9923

IF - Quantification of this coupound prohibited by interfering peak on GC/MS.

[a] Fast VOST sampling was conducted only during Runs 2 and 4.

[b] Incineration conditions were purposely altered from normal operation for Run 4 to obtain data on poor performance. The combustion temperature for Run 4 was 969°C (1776°F) versus an average temperature over Runs 1, 2, and 3 of 1067°C (1952°F).

TABLE 4-3. DESTRUCTION AND REMOVAL EFFICIENCIES (DREs) FOR THE UPJOHN INCINERATOR - BLANK CORRECTED

	Fast VOST		
Volatile compounds	Run 2	Run 3	Run 4
Carbon tetrachloride	99.9925	99.971	99.988
Trichloroethylene	> 99.9922	99.9914	99.9914
Chlorobenzene	99.937	99.910	99.956
Chloromethane	> 99.990	> 99.9916	> 99.9903

	MM5		
Semivolatile compounds	Run 2	Run 3	Run 4
m-Dichlorobenzene	99.922	99.905	99.932
o-Dichlorobenzene	99.9990	99.993	99.9990
p-Dichlorobenzene	99.9990	99.995	99.9990
1,2,4-Trichlorobenzene	99.65	98.6	99.75
Bis(ethyl hexy)phthalate	99.98	99.95	99.98
Phenyl isocyanate	> 99.99992	> 99.99990	> 99.99992
Aniline	[a]	> 99.9988	> 99.9991
Phosgene	99.9985	99.9930	99.981

[a] Waste feed concentration < 100 μg/g in this run.

TABLE 4-4. DESTRUCTION AND REMOVAL EFFICIENCIES (DREs) FOR THE ZAPATA INCINERATOR - BLANK CORRECTED

	Fast VOST	
Volatile compounds	Run 2	Run 3
Methylene chloride	> 99.906	[a]
Carbon tetrachloride	99.99911	99.9990
Trichloroethylene	99.9979	99.9985
Toluene	> 99.9914	> 99.9932
Chlorobenzene	> 99.9953	> 99.9974

[a] Waste feed concentration < 100 μg/g in this run.

TABLE 4-5. DESTRUCTION AND REMOVAL EFFICIENCIES (DREs) FOR THE AMERICAN CYANAMID INCINERATOR - BLANK CORRECTED

Semivolatile compounds	Aniline waste Run 2	Aniline waste Run 3	Aniline waste Run 5	Mononitrobenzene waste Run 4
Aniline	> 99.999989	> 99.999992	> 99.999992	> 99.9997
Phenylene diamine	> 99.997	> 99.9992	> 99.999	a
Diphenyl amine	> 99.999	> 99.9992	> 99.9992	a
Mononitrobenzene	a	a	a	99.99991
m-Dinitrobenzene	a	a	a	> 99.99

[a] Waste feed concentration < 100 μg/g in this run.

TABLE 4-6. DESTRUCTION AND REMOVAL EFFICIENCIES (DREs) FOR THE MITCHELL INCINERATOR - BLANK CORRECTED

Volatile Compounds	Fast VOST Run 1	Fast VOST Run 2	Fast VOST Run 3
Carbon tetrachloride	99.99966	99.99942	99.99946
Trichloroethylene	99.9975	99.9977	99.99906
Benzene	a	99.972	99.914
Tetrachloroethylene	a	a	> 99.9985
Toluene	> 99.9973	99.9926	99.9916
Methyl ethyl ketone	> 99.99957	99.99913	99.9979

Semivolatile compounds	MM5 Run 1	MM5 Run 2	MM5 Run 3
Phenol	99.9985	> 99.99996	> 99.9996
Naphthalene	99.96	99.98	99.986
Butyl benzyl phthalate	> 99.992	> 99.995	> 99.973
Bis (2-ethyl hexyl phthalate)	99.9985	99.993	99.996

[a] Waste feed concentration < 100 μg/g in this run.

TABLE 4-7. DESTRUCTION AND REMOVAL EFFICIENCIES (DREs) FOR THE DU PONT INCINERATOR - BLANK CORRECTED

Volatile compounds	Fast VOST		
	Run 1	Run 2	Run 3
Methylene chloride	99.99919	99.99954	99.9989
Chloroform	99.9929	99.989	99.9917
1,1,1-Trichloroethane	99.928	[a]	[a]
Carbon tetrachloride	99.99990	99.999928	99.99976
Trichloroethylene	99.99971	99.99975	99.9985
Tetrachloroethylene	99.99937	99.99960	99.99921
Toluene	99.99975	99.999926	99.999902
cis-1,4-Dichloro-2-butene	99.99971	> 99.999991	> 99.999991

Semivolatile compounds	MM5		
	Run 1	Run 2	Run 3
trans-1,4-Dichloro-2-butene	> 99.99990	> 99.99990	> 99.99992
Benzyl chloride	> 99.9996	> 99.9996	> 99.9994
Hexachloroethane	> 99.99	> 99.99	> 99.99
Naphthalene	98.0	99.10	97.4

IF - Quantitation prohibited due to interfering compound on GC/MS.

[a] Waste feed concentration < 100 μg/g in this run.

TABLE 4-8. DESTRUCTION AND REMOVAL EFFICIENCIES (DREs) FOR THE TWI INCINERATOR - BLANK CORRECTED

Volatile compounds	Fast VOST			
	Run 1	Run 2	Run 3	Run 4
Methylene chloride	> 99.918	99.71	99.88	99.63
Chloroform	> 99.944	98.2	97.8	99.78
Methylene bromide	> 99.9987	99.9956	99.964	99.982
1,1,1-Trichloroethane	99.966	99.81	99.86	99.82
Carbon tetrachloride	> 99.9984	> 99.9983	> 99.9987	> 99.99903
Trichloroethylene	> 99.9962	99.9945	99.9917	> 99.9989
Benzene	99.9983	99.989	99.984	99.988
Tetrachloroethylene	99.965	99.78	99.88	99.982
Toluene	99.99946	99.9908	99.9963	99.9922
Chlorobenzene	99.965	99.70	99.956	99.966

Semivolatile compounds	MM5			
	Run 1	Run 2	Run 3	Run 4
Hexachlorocyclopentadiene	> 99.99	> 99.99	> 99.99	> 99.9996
Bis(2-ethyl hexyl)phthalate	99.951	99.960	99.940	99.88
Chlordane	> 99.9998	> 99.9999	> 99.9999	[a]
Naphthalene	[a]	[a]	[a]	99.996
Hexachlorobutadiene	[a]	[a]	[a]	> 99.98

[a] Waste feed concentration < 100 μg/g in this run.

The DREs calculated from gas bags and slow VOST data are contained in the test reports (Appendices C through J).

In some cases the results reported in Tables 4-1 through 4-8 could not be explicitly quantified and less than (<) or greater than (>) values were calculated. The less than value occurs when the compound saturates the mass spectrometer and a lower bound mass on the trap is calculated. The greater than values occur when the mass measured on the stack sample cannot statistically be distinguished from the mass on the blank. In those cases an upper bound for the stack samples was established.

The DREs span a wide range for both volatile and semivolatile compounds. The 134 volatile and 106 semivolatile data points (a data point is one test run for one compound) are distributed as follows:

DRE Range	< 99	99-99.9	99.9-99.99	99.99-99.999	> 99.999
Volatiles (fast VOST)	2	12	30	51	39
Semivolatiles	3	5	20	46	32

DREs < 99.99% tend to occur when one or both of two factors are present. The first factor is low concentration in the waste feed (i.e., < 1,000 μg/g). The data show a trend of decreasing DRE with decreasing waste feed concentration. The second factor involves compounds which have been identified as PICs at other facilities (esp. chloroform, methylene chloride, benzene, and naphthalene). The formation of these compounds during the incineration of chlorinated organics would increase their concentration in the stack gas, resulting in a lower DRE. Eighty percent of the volatile points and 96% of the semivolatile points below 99.99% DRE occurred in cases where one or both of these factors were present. These two factors are discussed in greater detail in Sections 4.1.1.2.1 and 4.1.2, respectively.

Some observations from the data base are: (1) the eight facilities achieved an average DRE of 99.992% for all volatile compounds; (2) an average for semivolatile compounds cannot be calculated because over half the stack measurements were below detection limits. However, the only semivolatile compounds measured which did not consistently achieve at least 99.99% DRE were phenol, bis(2-ethylhexyl)phthalate, diethyl phthalate, naphthalene and m-dichlorobenzene; (3) based on volatile DREs the plants which had the best performance were a parallel rotary kiln/liquid injection unit (Du Pont), a liquid injection/hearth unit (Zapata), and a liquid injection unit (Mitchell); (4) the lowest volatile DREs were recorded at two liquid injection units, Plant B and Upjohn; and (5) only one liquid injection/hearth unit (Zapata) and one liquid injection unit (American Cyanamid) achieved an average DRE of 99.99% for all semivolatile and volatile POHCs. These observations can be compared to the process descriptions in Section 3.4, however, no correlations with process parameters were identified.

4.1.1.2 Findings Concerning Factors Thought to Have an Impact on DREs--

A number of factors are thought to contribute to the achievement or failure of a desired destruction and removal efficiency. The data base has been analyzed to determine the influence on DREs of such factors as waste feed concentration, heat of combustion, operating conditions (such as temperature and residence time), and noncombustion mechanisms (such as control equipment and inleak air). The results of these analyses which, because of the number of facilities tested and the variety of designs and conditions at each, cannot be considered definitive are presented below.

4.1.1.2.1 Relationship between DRE and waste feed concentration--To explore the possible relationship between DRE and POHC concentration in the waste feed, the blank corrected value for penetration was calculated for each of the points in the data base, where:

$$\text{Penetration} = \frac{W_{out}}{W_{in}} = 1 - \frac{DRE}{100}$$

The waste feed concentration was calculated by dividing the mass input rate for the POHC by the total mass input rate of all waste feed streams to an incinerator. The values were used to construct a plot of penetration versus waste feed concentration, which exhibited a linear configuration on log/log coordinates (see Figure 4-1).

Linear regression showed that the data were best fit by a line with a slope of -0.79. As can be seen from Figure 4-1, no compounds below 200 μg/g in the waste feed achieved a DRE greater than 99.99%. Only one compound below 1,000 μg/g in the waste feed achieved a DRE greater than 99.99%. Only three points above 10,000 μg/g did not achieve a DRE greater than 99.99%, and no points above 12,000 μg/g failed to achieve 99.99% DRE. The correlation coefficient of -0.84 for the regression line is highly significant.

The trend of decreasing DRE with decreasing waste feed concentration was also tested on a plant-by-plant and compound-by-compound basis. The results are presented in Tables 4-9 and 4-10. TWI and Du Pont were the two plants with the most quantifiable data points. The linear regression lines for these two plants are shown in Figures 4-2 and 4-3, respectively. All the plants reflected this trend, although Upjohn had a much lower correlation coefficient. All of the compounds except trichloroethylene also reflected this trend.

Trichloroethylene and carbon tetrachloride were both spiked into the waste feeds which resulted in a relatively narrow range of waste feed concentrations (less than two orders of magnitude). This narrow range may account for the low correlation coefficients for these two compounds.

A similar comparison using the data for semivolatile POHCs showed the same basic relationship (see Figure 4-4). A correlation coefficient of -0.76, which statistically is highly significant, was obtained.

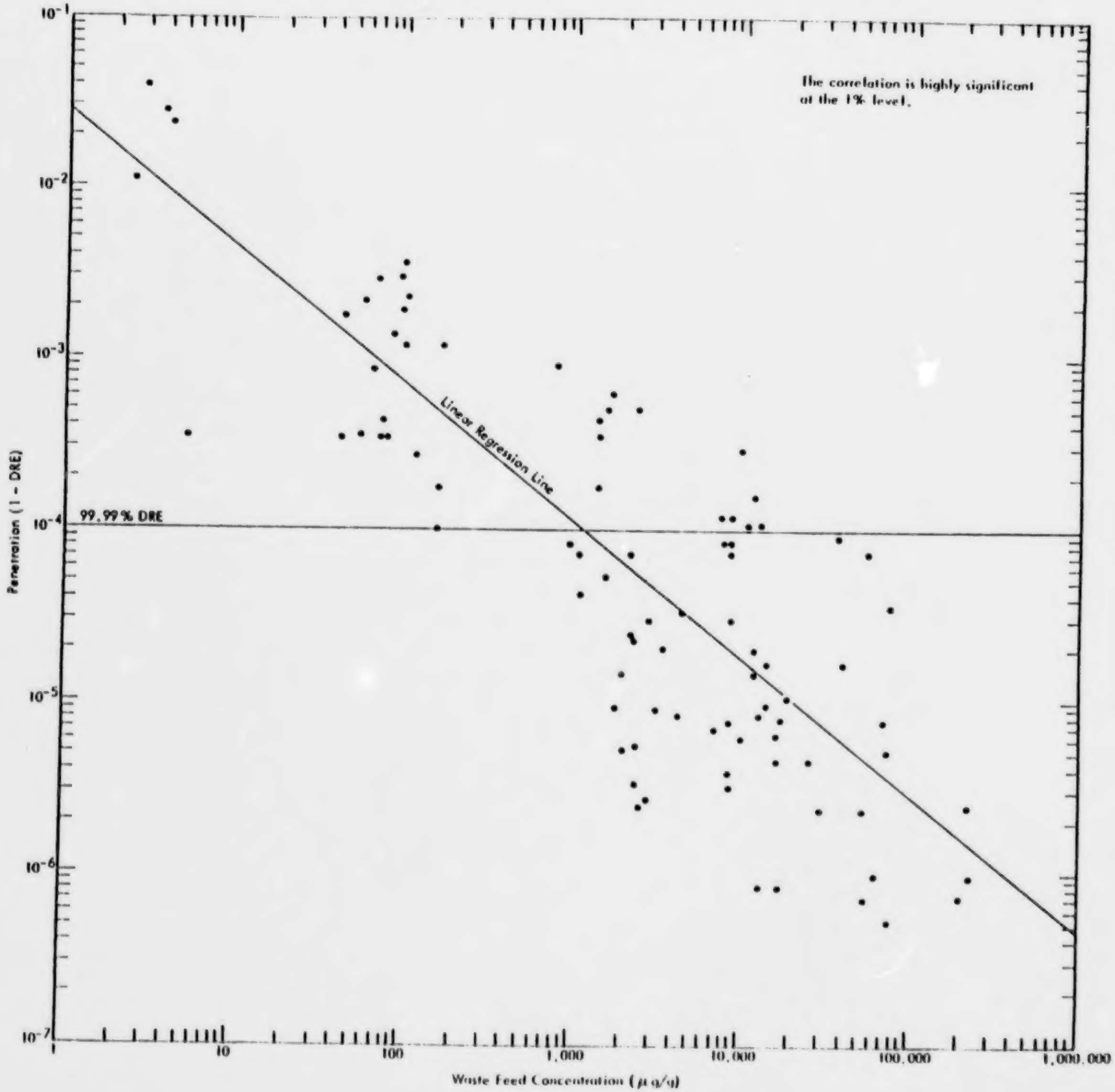


Figure 4-1. Penetration versus waste feed concentration - volatiles (fast VOST) - best available blank correction points.

TABLE 4-9. LINEAR REGRESSION RESULTS BY PLANT FOR LOG PENETRATION VERSUS LOG WASTE FEED CONCENTRATION (FAST VOST)

Plant*	No. of points	Correlation coefficient	Slope	Intercept (penetration at the 1 μg/g level)
TWI	28	-0.81	-0.52	0.0085
DuPont	15	-0.67	-0.42	0.0002
Mitchell	13	-0.94	-0.97	0.026
Upjohn	11	-0.14	-0.09	0.0003
Total	85	-0.84	-0.79	0.026

* Only the plants having more than 10 points in the total correlation are displayed here.

TABLE 4-10. LINEAR REGRESSION RESULTS BY COMPOUND FOR LOG PENETRATION VERSUS LOG WASTE FEED CONCENTRATION (FAST VOST)

Compound	No. of points	Range of waste feed concentrations (μg/g level)	Correlation coefficient	Slope	Intercept (penetration at the 1 μg/g level)
Toluene	15	2.5-220,000	-0.95	-0.77	0.054
Trichloroethylene	14	1,600-12,000	0.22	0.33	0.0000014
Carbon tetrachloride	11	2,000-62,000	-0.34	-0.53	0.0013
Tetrachloroethylene	9	53-17,000	-0.88	-0.89	0.040
Methylene chloride	6	59-19,000	-0.99	-1.1	0.44
Total	85	2.5-220,000	-0.84	-0.79	0.026

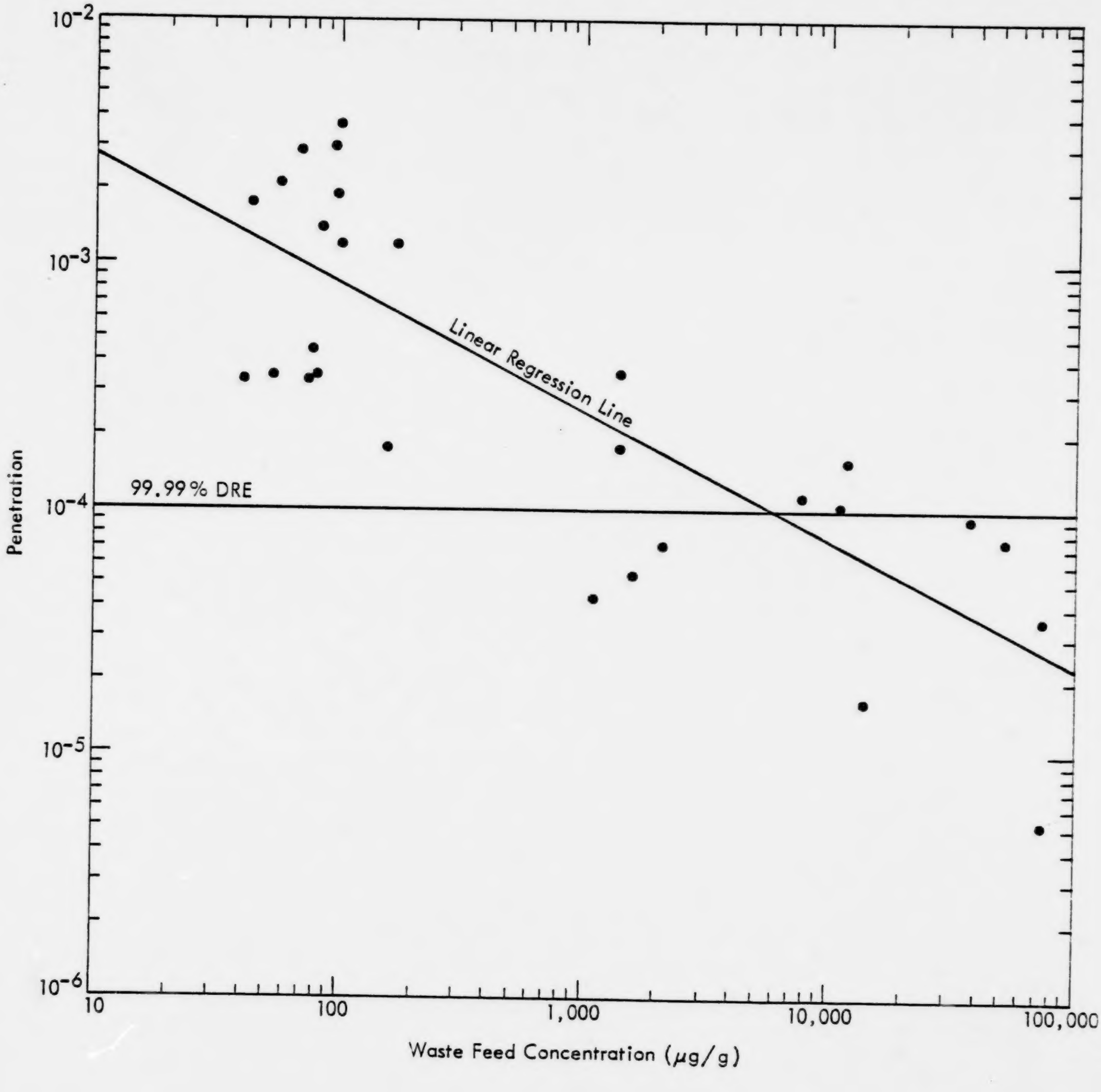


Figure 4-2. Penetration versus waste feed concentration - volatiles (fast VOST) - TWI.

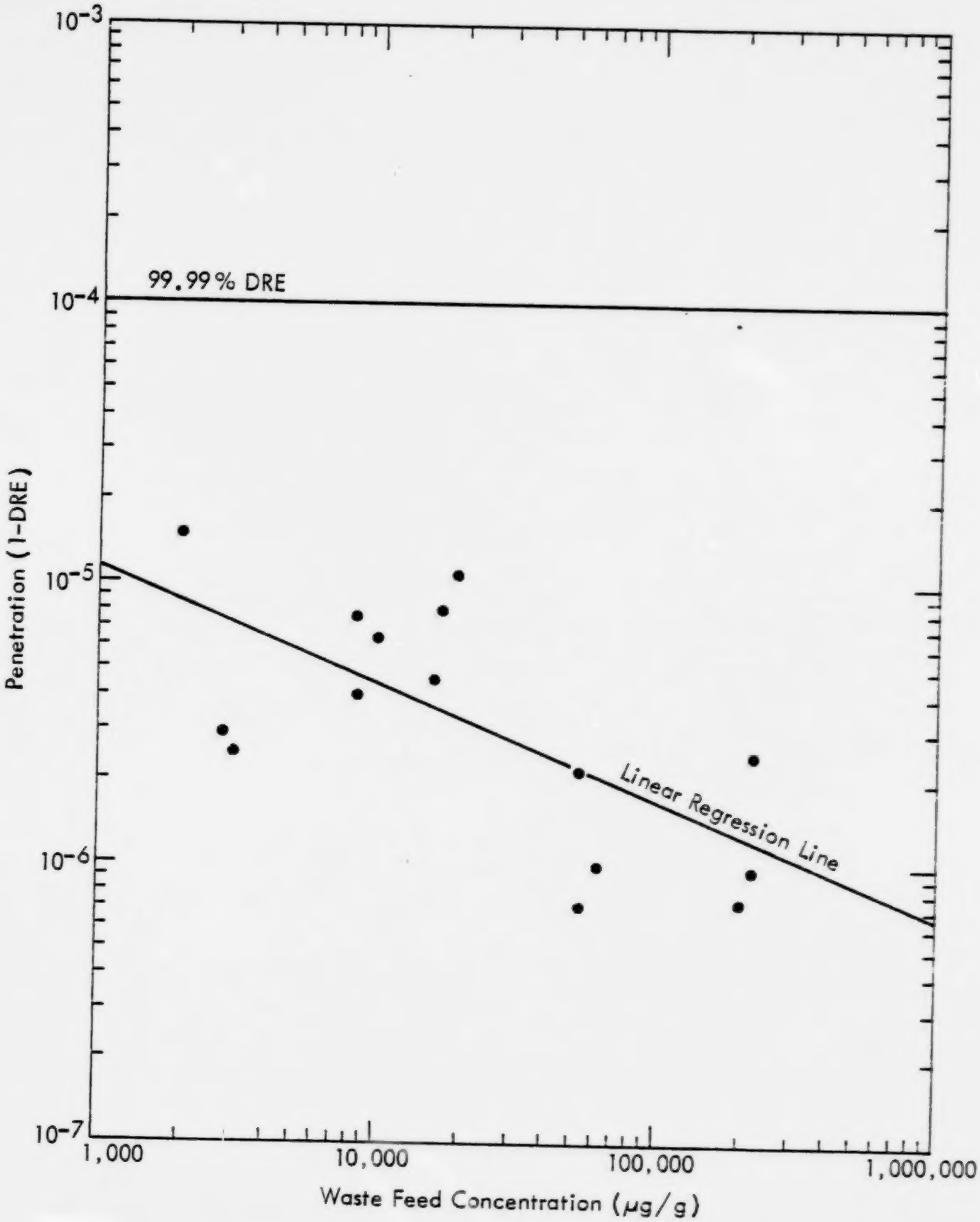


Figure 4-3. Penetration versus waste feed concentration - volatiles (fast VOST) - Du Pont

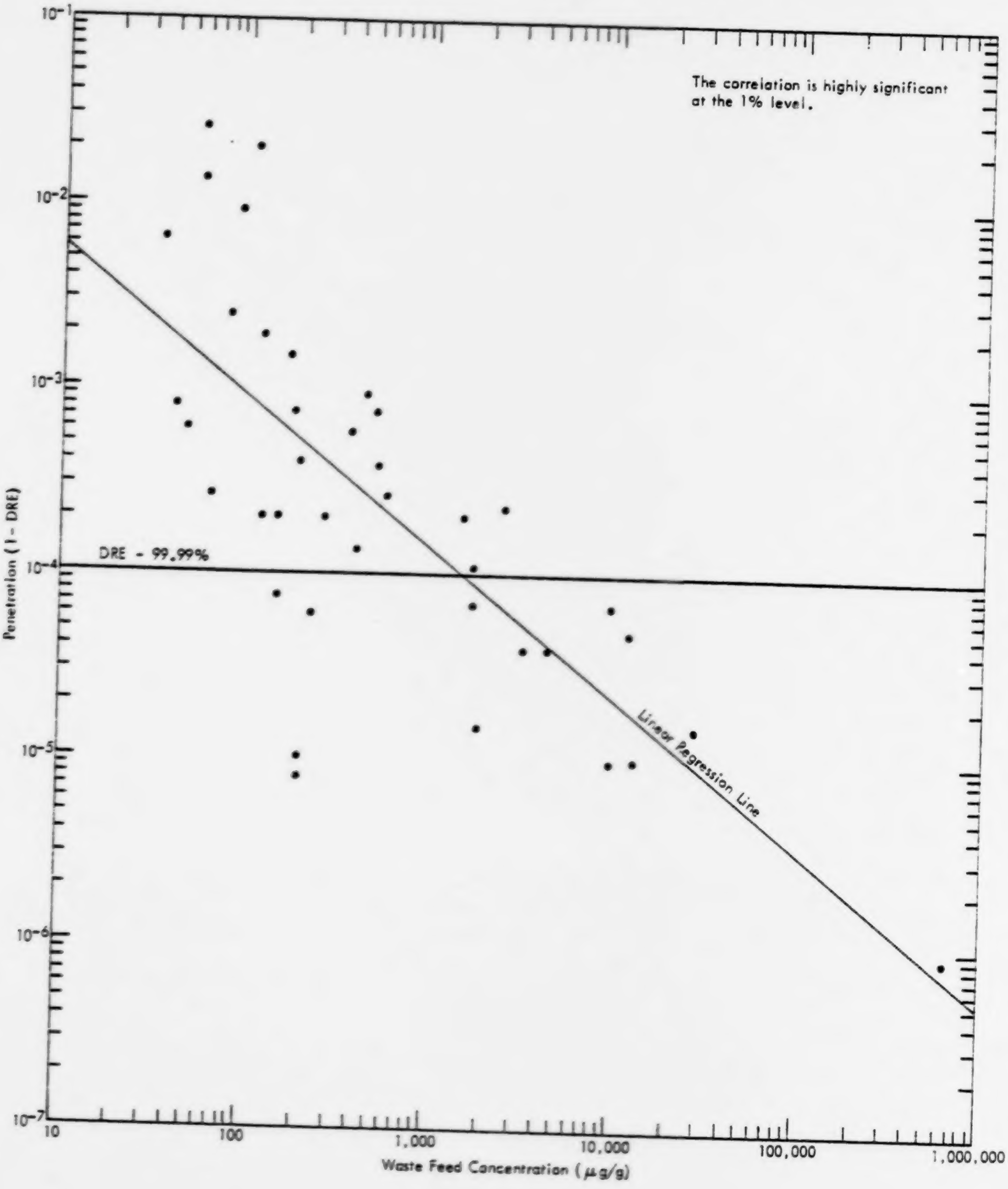


Figure 4-4. Penetration versus waste feed concentration - semivolatiles - blank corrected data.

To further investigate the trend established above, the data were analyzed from two additional points of view. First, the data base was expanded to include all points in order to determine if the blank correction process biased the data base by eliminating points which fell near the detection limit. An additional 33 points were added to the volatile POHC data base. A comparison of the linear regression fit for the two groups is presented in Table 4-11. The slopes for the two groups did not differ significantly and both correlation coefficients were highly significant.

TABLE 4-11. COMPARISON OF DATA BASED FOR VOLATILES BY VOST METHOD

	No. of points	Correlation coefficient	Slope	Intercept
Log penetration versus log concentration				
Including all data	112	-0.70	-0.73	2.0
Most reliable data	85	-0.84	-0.79	2.4

The range of waste feed concentrations represented by this trend was extended by examining waste feed analyses for compounds which might have been present in feed streams at low concentrations (< 100 μg/g). For three of the facilities, American Cyanamid, Mitchell, and TWI, waste feed concentrations down to 1 μg/g were measured for some of the waste feed streams. When DREs are calculated for these low concentration compounds, the values fall into place along the same trend shown by POHC compounds. These values are presented in Table 4-12.

A similar expansion of the semivolatile data base was not possible. All of the additional points were "less than" values which represented the detection limit for the compounds in the stack. Since these values can not be quantified, there is no suitable way to add them into the data base. These nonquantifiable values represent "greater than" DREs resulting from stack concentrations below detection limits. Typically, these DREs would be > 99.995.

A second analysis comparing stack gas concentration with inlet concentration was conducted (see Figure 4-5). From the log penetration versus log waste feed concentration plot a relationship can be derived relating outlet concentration to inlet concentration. When the most reliable VOST data are plotted, linear regression confirms this relationship, further supporting the dependence of DRE on waste feed concentration. (Note that the 99.99% DRE band in Figure 4-5 is a result of the range in the ratio of stack gas flow rate to waste mass feed rate.)

TABLE 4-12. DREs CALCULATED FOR SELECTED PIC COMPOUNDS

Plant/run		Compound	Overall waste feed concentration (μg/g)	Output rate (g/min)	DRE
Mitchell	1	Methylene chloride	4.8	0.000046	99.90
	2		17	0.00028	99.82
	3		38	0.00012	99.96
	1	Chloroform	6.1	0.000095	99.84
	2		4.7	0.00045	99.66
	3		3.1	0.000094	99.70
	1	1,1,1-Trichloroethane	1.1	< 0.000005	> 99.95
	2		1.3	0.000015	99.88
	3		< 0.56	< 0.000005	-
TWI	1	Chlorobromomethane	0.6	0.000065	99.35
	2		6.8	0.00084	99.12
	3		6.2	0.0010	98.8
	4		5.4	0.0011	97.7
American Cyanamid	1	Toluene	2.9	0.00029	95.9
	2		4.3	0.00015	97.9
	3		3.7	0.00020	97.6
	4		2.5	0.00008	99.0

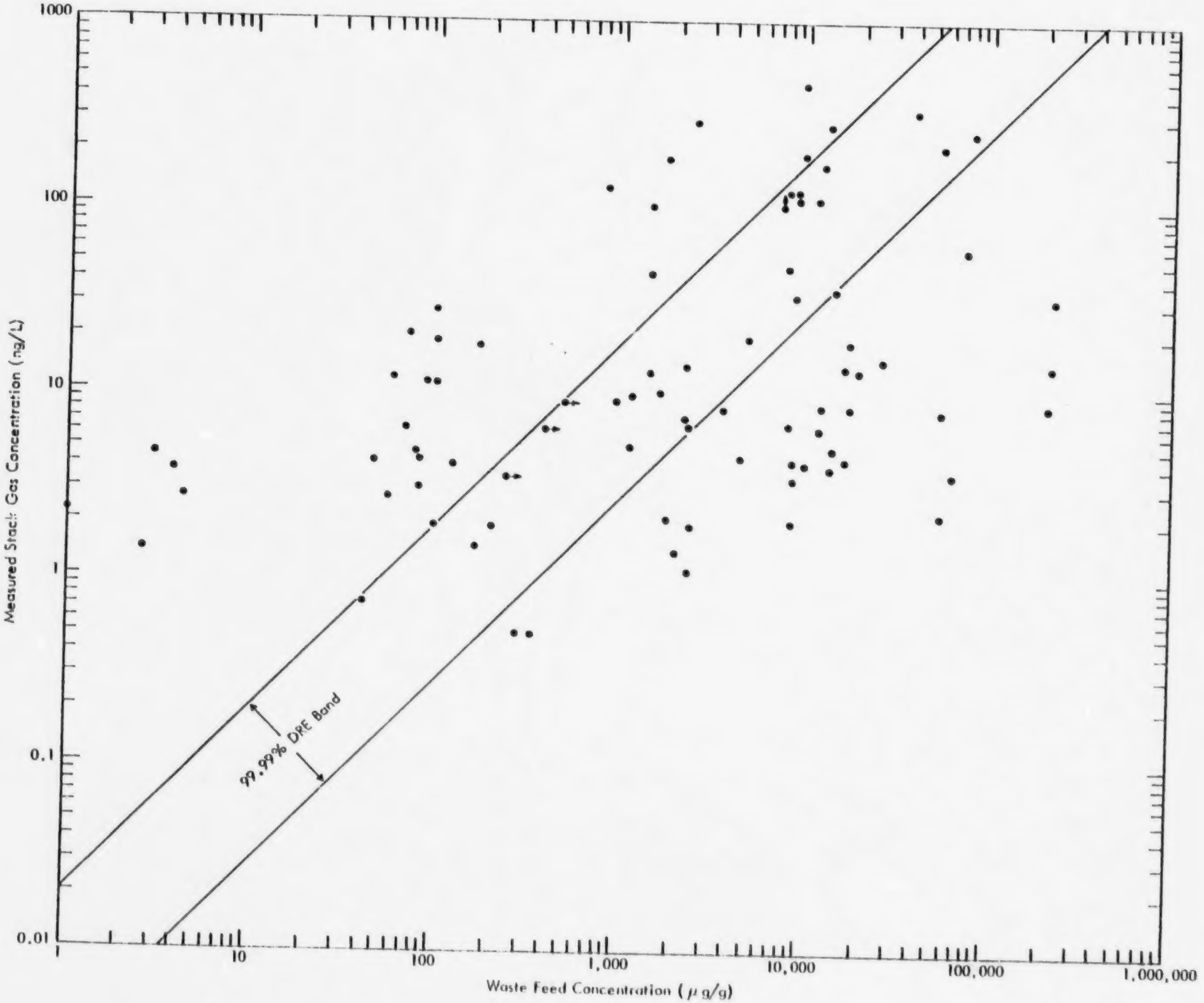


Figure 4-5. Stack concentration versus waste feed concantration - volatiles (fast VOST) - best available blank corrected points.

The relationship suggested by this analysis conflicts with the traditional assumption that DRE remains constant regardless of waste feed concentration. That assumption follows from use of a first order combustion reaction equation to represent incinerator performance. Variation of DRE with waste feed concentration is more reflective of the relationship predicted by rate expressions higher than first order, as discussed below.

The integrated expression for a first order reaction with respect to the compound A takes the following form:

$$\ln \left(\frac{C_{out}}{C_{in}}\right) = -kt \qquad (1)$$

where

C_{out} = concentration of A in the gas exiting the combustion chamber

C_{in} = concentration of A in the gas entering the combustion chamber

k = reaction rate constant (a function of temperature, T, and compound specific characteristics)

t = residence time

Taking the exponential of both sides of Eq. (1) and rearranging yields:

$$C_{out} = e^{-kt} C_{in} \qquad (2)$$

For a given temperature and residence time the outlet concentration is predicted by the equation as directly proportional to the inlet concentration. This would indicate that DRE is independent of waste feed concentration.

The integrated expression for a reaction which is not first order with respect to A (where n is the order of reaction) appears as follows:

$$\frac{1}{n-1}\left[\frac{1}{C_{out}^{n-1}} - \frac{1}{C_{in}^{n-1}}\right] = kt \qquad (n \neq 1) \qquad (3)$$

For a second order reaction (n = 2) Eq. (3) reduces to

$$\frac{1}{C_{out}} - \frac{1}{C_{in}} = kt \qquad (4)$$

For a reaction with a DRE near 99.99%

$$C_{in} >> C_{out}$$

and

$$\frac{1}{C_{in}} << \frac{1}{C_{out}} \tag{5}$$

In this case Eq. (4) can be expressed

$$\frac{1}{C_{out}} \cong kt \tag{6}$$

For a given temperature and time the equation predicts an outlet concentration that is virtually independent of the inlet concentration. Consequently, penetration would be inversely correlated to inlet concentration. The relationship predicted by such an equation more closely resembles the relationship identified in the test data but still is not adequate for predicting performance.

This same relationship would be the result of any reaction higher than first order. To establish the order of the reaction for a specific compound, a good set of data would be required for various times and temperatures for each compound, but with all other parameters that affect DRE held constant. The data collected during this program were from eight incinerators that have varying characteristics other than time and temperature that affect the combustion reaction, thus these data are not adequate to determine orders of reactions.

This analysis does not exclude the possibility of first order reactions (or any order reaction) occurring for some compounds in the combustion chamber. Rather, the analysis suggests that the overall incineration process--from waste feed to stack gas--is more accurately represented by a higher-than first order rate expression.

The data from these incinerator tests indicate a strong trend of increased DRE with increasing waste feed concentrations, both for volatiles and semivolatiles. This phenomenon is supported on a plant-by-plant and a compound-by-compound basis. Volatile POHCs did not achieve 99.99% DRE at waste feed concentration of 100 μg/g. At high concentrations (> 12,000 μg/g), all of the compounds achieved 99.99% DRE.

4.1.1.2.2 Relationship between DRE and heats of combustion--The relationship between DRE and the heat of combustion of a POHC was examined by using Spearman's rank order correlation (r_{sp}), a nonparametric method that provides similar information to that provided by Pearson's correlation coefficient (r). The principal advantage of the nonparametric method is that it requires neither normally distributed data nor a linear relationship. It will demonstrate a positive monotonic relationship between the two variables.

The rank order correlation coefficient was calculated for four of the final five incinerator tests (Zapata, Mitchell, Du Pont, and TWI). The first three tests were not used because of uncertainties in the DREs caused by blank problems. The data from American Cyanamid were not used because only one of the five POHCs in the waste was detected in the stack gas making statistical analysis impossible. Since the compounds used for each plant cover a broad range of heats of combustion, the elimination of the non-detected compounds did not severely impact the analysis.

If the incinerability of a compound were dependent on its heat of combustion, the DREs for compounds subject to the same incinerator conditions should be positively correlated with the heats of combustion of those compounds. As shown in Table 4-13 none of the data for the four plants show a significant positive correlation, and two of the four show a negative correlation that was significant. Data which were normalized to account for the effect of inlet feed concentration still showed no significant correlation between DRE and heats of combustion.

Data from this program do not support heat of combustion alone as an indicator of incinerability. Alternate methods to assess incinerability should be considered. This conclusion is supported by an earlier theoretical analysis which showed no relationship between the 99% destruction temperature and heat of combustion.[1]

4.1.1.2.3 Relationship between DRE and operating conditions--The degree to which relationships between DRE and incinerator or waste feed characteristics could be defined was severely limited by the type of data base compiled during the program. Since blank problems were encountered during the first three tests, complete data sets were only available for the last five tests. Given the number of incinerator parameters which can affect DREs, these five basic sets of conditions provide a small basis for analyzing the impacts of multiple variables. Further, site selection was random rather than based on an experimental design aimed at investigating specific operating conditions. Because of these limitations, the results described below should be viewed with caution. The results only indicate relationships which warrant further consideration; they are not sufficient to establish definitive relationships between DRE and operating conditions.

A multivariate analysis using data for six compounds at five facilities was conducted to determine what factors had an impact on the variance of DRE. Residence time, chamber temperature, heat input rate, and stack O_2 concentration were the four operating conditions used in the analysis. Of the four, only temperature showed a marginal correlation with DRE.

A discriminant analysis using the same data base was also conducted. The discriminant analysis is a multivariate technique that develops a function which predicts one variable in terms of a group of other variables and classifies the initial variable in one or more classes. In this case the dependent variable was DRE and the classes were to achieve 99.99% DRE or fail 99.99% DRE. This analysis indicated that temperature and inlet POHC concentrations were the primary factors in a discriminant function which accurately predicts the achievement or failure of a 99.99% DRE.

TABLE 4-13. RANK ORDER CORRELATION (r_{sp}) OF DRE TO HEATS OF COMBUSTION

Compound	Heat of[a] combustion (kcal/g)	Relative DRE ranking[b]			
		Zapata	Mitchell	Du Pont	TWI
Carbon tetrachloride	0.24	5	9	6	11
Methylene bromide	0.50				6
Tetrachloroethylene	1.19			4	3
Methylene chloride	1.70	1		3	1
Trichloroethylene	1.74	4	3	2	9.5
1,1,1-Trichloroethane	1.99				2
cis-1,4-Dichloro-2-butene	4.27			5	
Chlorobenzene	6.60	3			4
Phenol	7.78		8		
Methyl-ethyl-ketone	8.07		7		
Butylbenzylphthalate	8.29		4		
bis(2 ethylhexyl)phthalate	8.42		6		5
Naphthalene	9.62		2	1	9.5
Benzene	10.03		1		7
Toluene	10.14	2	5		8
	r_{sp}	-0.4	-0.58[c]	-0.66[c]	-0.10

---

[a] Compounds are listed in order with lowest heat of combustion.

[b] These rankings represent the relative order of the DREs with 1 - lowest DRE; 2 - second lowest DRE; etc.

[c] Significant at the 10% level, i.e., correlation coefficients of this magnitude would be obtained by chance only 10% of the time.

The data compiled during this program suggest that other factors (i.e., waste feed concentration, specific compound kinetics, PIC formation) have a greater impact on DRE than residence time, heat input and stack O_2 concentration. Furthermore, the plant-to-plant differences in the measurement of temperature and determination of residence times complicate identification of relationships between these parameters and DREs or other indicators of performance. However, the data do suggest that temperature may have a significant impact on DRE. Further controlled experiments to evaluate that relationship appear to be warranted.

Overall, the data suggest that prediction of performance (as defined by achievement of 99.99% DRE) for the particular incinerators tested on this program, based on evaluation of commonly measured incinerator operating or design parameters may not be reasonable. For example, Zapata which had a small combustion chamber, minimal controls, and a short residence time provides "best" performance using 99.99% DRE as a criteria while Plant B, with a high level of combustion control and reasonable residence times and temperatures, provides poorer performance.

4.1.1.2.4 Effects of noncombustion mechanisms on destruction/removal of POHCs--This section discusses the effects of noncombustion mechanisms on DREs for POHCs. Specific mechanisms discussed include removal of POHCs with incinerator bottom ash, absorption of POHCs in or stripping of POHCs from scrubber liquids, and contribution of inleak air to POHC mass emission rates.

Incinerator ash was examined to determine the fraction of POHCs removed in the ash. Only two facilities had concentrations of POHCs of greater than 35 μg/g in the ash. Chlordane was detected in concentrations ranging from 60 to 570 μg/g in chamber solids at TWI when chlordane-contaminated sand and gravel was used as a waste feed. This quantity represented 0.3 to 3% of the concentration in the waste feed. Naphthalene was detected in the ash at the Ross incinerator at a concentration of 67 μg/g. For all other facilities, the highest concentration level in an ash sample of any POHC (toluene at 35 μg/g) accounted for only 0.0004% of the amount fed to the incinerator. When POHCs were detected in ash they tended to be toluene, phenol, or naphthalene at low concentrations (less than 10 μg/g). These data suggest that in cases where POHCs are mixed in noncombustible solids at concentrations of 1% or less, the ash may be a significant removal mechanism.

Scrubber waters were analyzed for POHCs at the five facilities which had wet scrubbers to determine if there was any removal of organics from the gas stream. Naphthalene was detected at 35 μg/L in the scrubber effluent at Plant B. For all other facilities, the POHCs detected in scrubber waters were usually toluene, phenol or naphthalene at concentrations below 20 μg/L. N,N-Dimethylacetamide, which is not a POHC, was present in a high concentration in the waste feed at Ross. This compound is highly soluble in water and was found in recycled scrubber effluent at a concentration of about 220 μg/L, the highest value for an organic compound in a scrubber effluent at any of the five facilities. This was the only instance in the series of tests that removal of an organic compound by a control device may have been a potential contributor to DRE. However, since the N,N-dimethylacetamide may have built up in the scrubber system over time, the percent removal could not be calculated. On balance, scrubbers do not appear to significantly increase DRE.

In several cases the control system contributed to the concentration of POHCs in the stack gas. At three facilities (TWI, Du Pont, and Plant B), the inflow water contained measurable concentrations of chloroform (~ 100 μg/L) and the outflow water contained no measurable chloroform (< 1 μg/L). This difference suggests that the chloroform was stripped from the waters and carried out by the stack gas. In all three cases, all of the chloroform detected in the stack can be accounted for by the chloroform in the inflow water. For this reason chloroform is considered a special case for facilities with water quenching or wet scrubbers, and it has been excluded from most of the analyses concerning DREs. In addition to chloroform, inflow waters appear to contribute smaller quantities of other trihalomethanes (bromoform, bromodichloromethane and dibromochloromethane) to the stack effluent at the facilities tested.

Another possible source of POHCs in the stack gas may be air which enters the negative pressure system after the combustion chamber. Heat balance calculations (presented in Section 4.3.) indicate that up to 50% of the air in the stack may be inleak air, entering after the combustion chamber. Any POHCs in this in-leak air would increase the mass emissions of those POHCs measured in the stack and decrease DRE, since any POHCs introduced by this air would be picked up in the sampling train. The possible effects of inleak air on POHC emissions have been explored at Du Pont, where ambient air concentrations of POHCs were measured. Using the inleak rate of 23% (as calculated from the heat balance) and assuming that the inleak air has the same concentrations of compounds as the ambient air near the stack, the relative contribution of the compounds from the inleak air can be calculated. For POHC compounds the inleak air could account for 1 to 100% of the total output. The 100% figure is for 1,1,1-trichloroethane, a POHC which was detected in low concentrations in the stack.

With the few exceptions noted earlier in this subsection, the data from these tests did not indicate any case that removal of POHCs through ash or scrubber effluent played a significant role in determining destruction and removal efficiencies. However, addition of POHCs from stripping of scrubber waters or from inleak air can act to decrease DRE in specific cases.

4.1.2 PICs

For this program PICs and POHCs are both Appendix VIII compounds. A PIC is any such compound detected in the stack gas which was not detected in the waste feed in concentrations greater than 100 μg/g. A POHC is an Appendix VIII compound which was detected in any waste feed at concentrations greater than 100 μg/g.

The available information compiled during this program on PIC emissions is presented in the four subsections below. The first subsection presents data on PIC emissions and compares those emissions to POHC emissions at the eight facilities tested. In the second and third sections possible mechanisms for PIC emissions are identified, and the potential contributions by each mechanism is evaluated. The final subsection contains information on two families of PICs that are of particular interest--dioxins and furans. We believe for the same reasons stated regarding the data on DREs, that one should not attempt to draw definitive conclusions from this information on PICs.

4.1.2.1 Summary of Information on PICs--

Approximately 30 compounds were classified as PICs from the eight tests (see Table 4-14). They were detected over a wide range of stack gas concentrations. Certain compounds were present in most or all of the stacks, either as POHCs or as PICs. These compounds make up a list of the hazardous organics which are most likely to be actual products of the incomplete combustion of hazardous constituents. The concentrations for the 14 most common compounds in the stack gas are presented in Figure 4-6.

The concentrations of PICs at the eight different facilities are presented in Figure 4-7. The PICs are divided into three categories: volatiles; semivolatiles; and trihalomethanes (THM's: chloroform, bromodichloromethane, dibromochloromethane, and bromoform). Trihalomethanes are not included in the totals due to the possibility that they may be contributed by the scrubbing systems at some facilities. Total PIC levels are compared to total POHC levels for the eight facilities in Figure 4-8. On the average, the PIC levels are slightly higher than the POHC levels, although this relationship varies widely from facility to facility. Calculations were carried out to determine PIC output rates as a percentage of the POHC input rates, and the results are presented in Table 4-15. At only one of the eight tests (Upjohn) were PIC output rates greater than 0.01% of POHC input rates.

4.1.2.2 Possible Mechanisms to Explain the Presence of PICs--

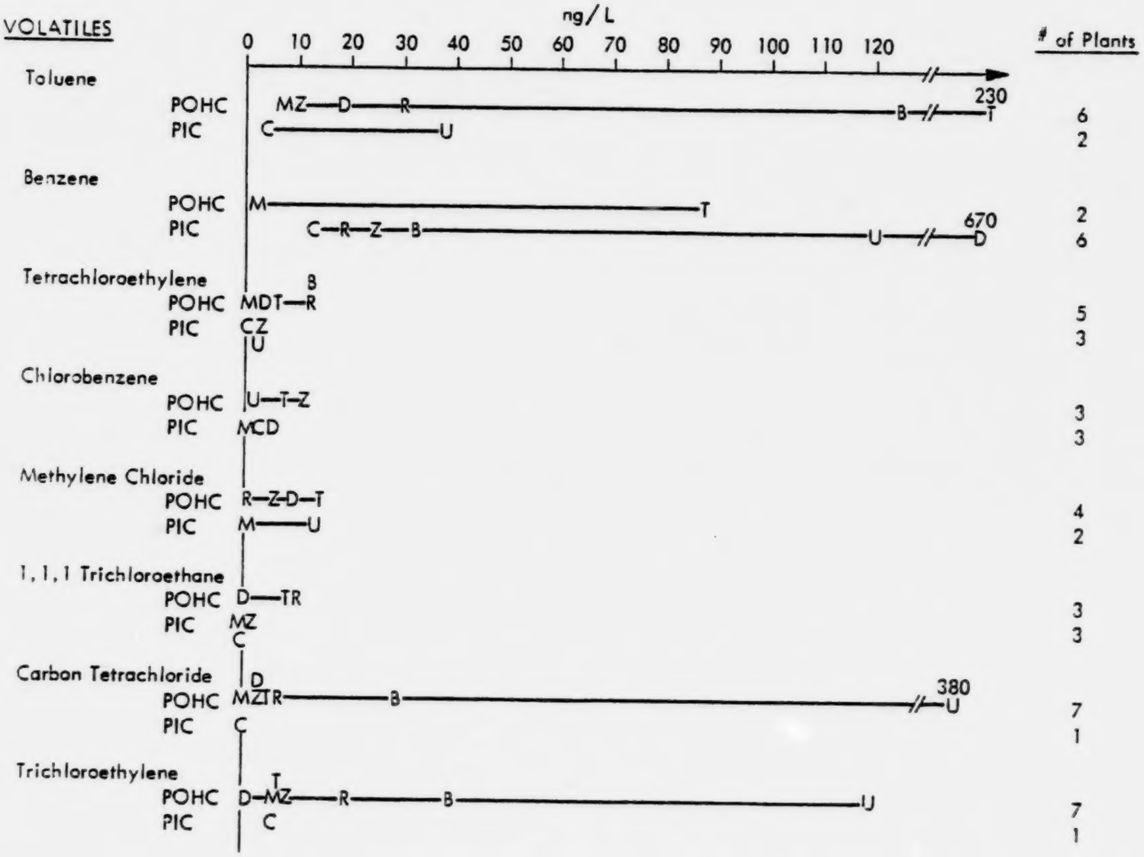
Three suggested explanations for the presence of PIC compounds are: (a) the compounds were actually present at low concentrations (< 100 μg/g) in the feed and were destroyed at a relatively low DRE; (b) the compounds were introduced to the system from some source other than the waste; and (c) the compounds are formed as products of combustion reactions.

4.1.2.2.1 PICs present in waste feed below 100 μg/g--The estimated stack concentration for a compound present in the waste feed just below the POHC limit of 100 μg/g and subject to a DRE of 99.9% is 10 ng/L. As explained in Section 4.1.1.2.1, this low DRE becomes very plausible when the trend of DRE versus concentration in waste feed is examined. The trend of decreasing DREs shows that many of the PICs detected could be explained by low concentrations in the feed.

For three facilities, American Cyanamid, Mitchell, and TWI, waste feed concentrations down to 1 μg/g were measured for some waste feed streams. The DREs for these compounds were consistent with the values predicted from POHC analysis. These data suggest that low concentrations of Appendix VIII constituents in the waste feed can be one source of PICs.

TABLE 4-14. PICs FOUND IN STACK EFFLUENTS

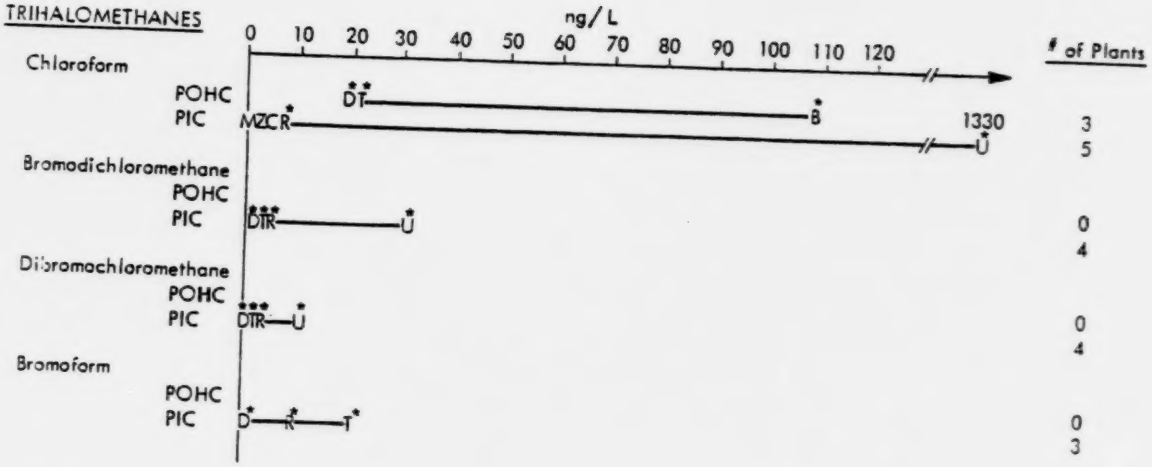
PIC	Number of sites	Concentrations (ng/L)
Benzene	6	12-670
Chloroform	5	1-1,330
Bromodichloromethane	4	3-32
Dibromochloromethane	4	1-12
Bromoform	3	0.2-24
Naphthalene	3	5-100
Chlorobenzene	3	1-10
Tetrachloroethylene	3	0.1-2.5
1,1,1-Trichloroethane	3	0.1-1.5
Hexachlorobenzene	2	0.5-7
Methylene chloride	2	2-27
o-Nitrophenol	2	25-50
Phenol	2	4-22
Toluene	2	2-75
Bromochloromethane	1	14
Carbon disulfide	1	32
Methylene bromide	1	18
2,4,6-Trichlorophenol	1	110
Bromomethane	1	1
Chloromethane	1	3
Pyrene	1	1
Flouranthene	1	1
Dichlorobenzene	1	2-4
Trichlorobenzene	1	7
Methyl ethyl ketone	1	3
Diethyl phthalate	1	7
o-chlorophenol	1	2-22
pentachlorophenol	1	6
2,4 dimethyl phenol	1	1-21



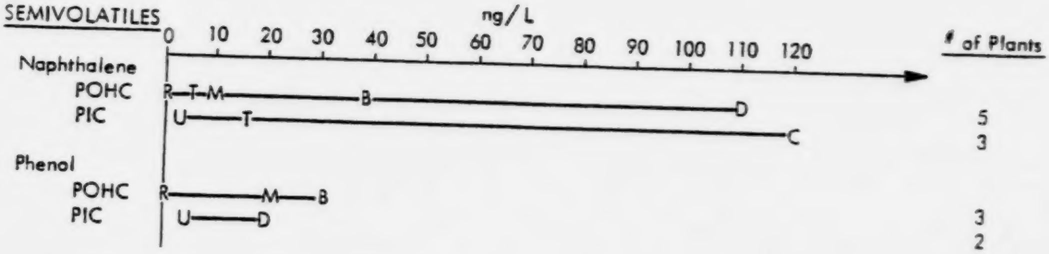
Plant Symbols:

R - Ross
B - Plant B
U - Upjohn
Z - Zapata
C - American Cyanamid
M - Mitchell
D - Du Pont
T - TWI

Figure 4-6. POHC and PIC concentrations in the stack for 14 most common compounds.

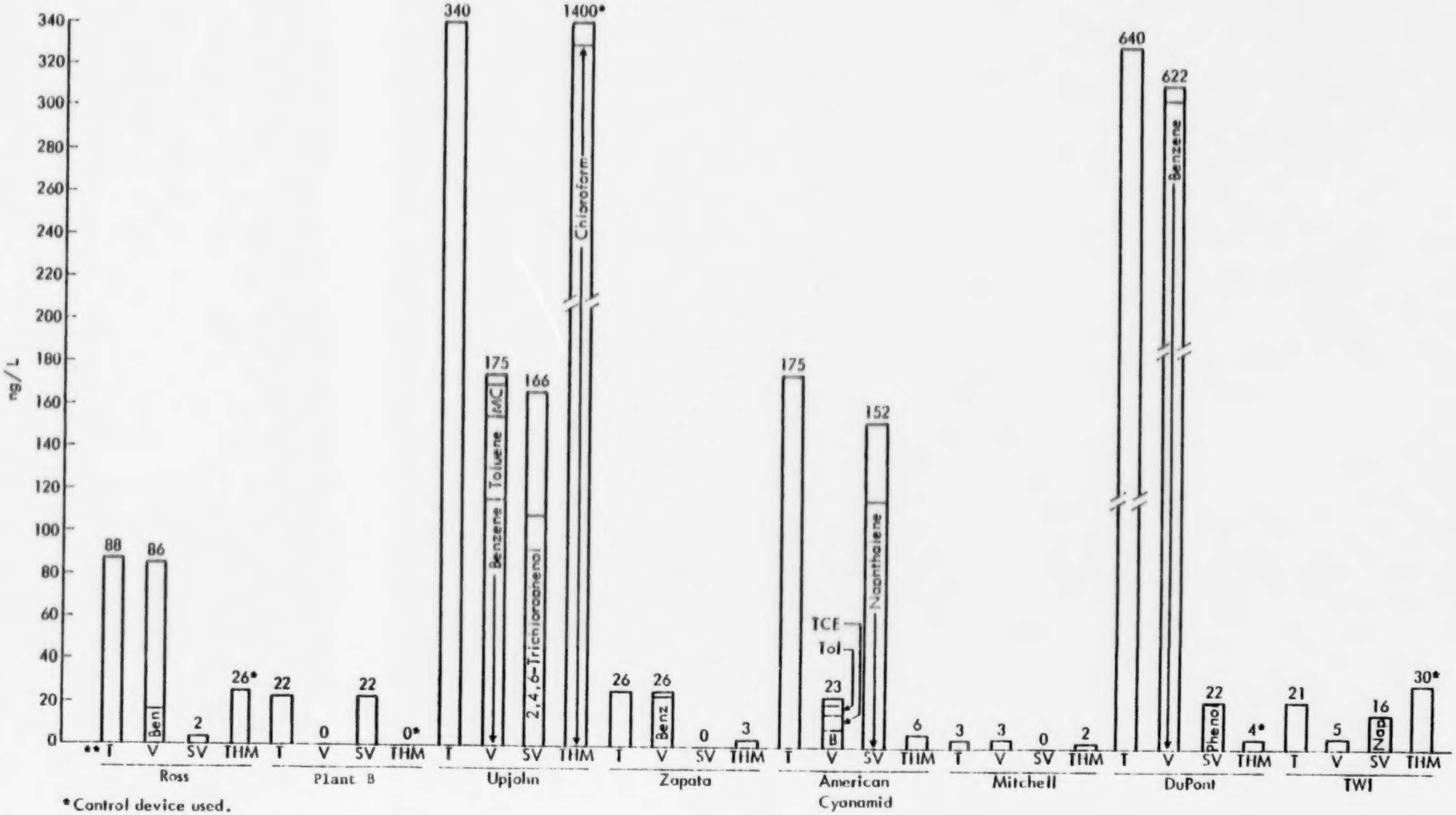


* Indicates plant with control device.



Note: Only 7 plants were analyzed for semivolatiles. Naphthalene appeared as both a PIC and a POHC at TWI.

Figure 4-6. (continued)



*Control device used.

** T = Total, V = Volatile SV = Semivolatile
THM = Trihalomethanes - chloroform, bromoform, bromodichloromethane, dibromochloromethane (not included in other totals).

Figure 4-7. Summary of average PIC concentrations.

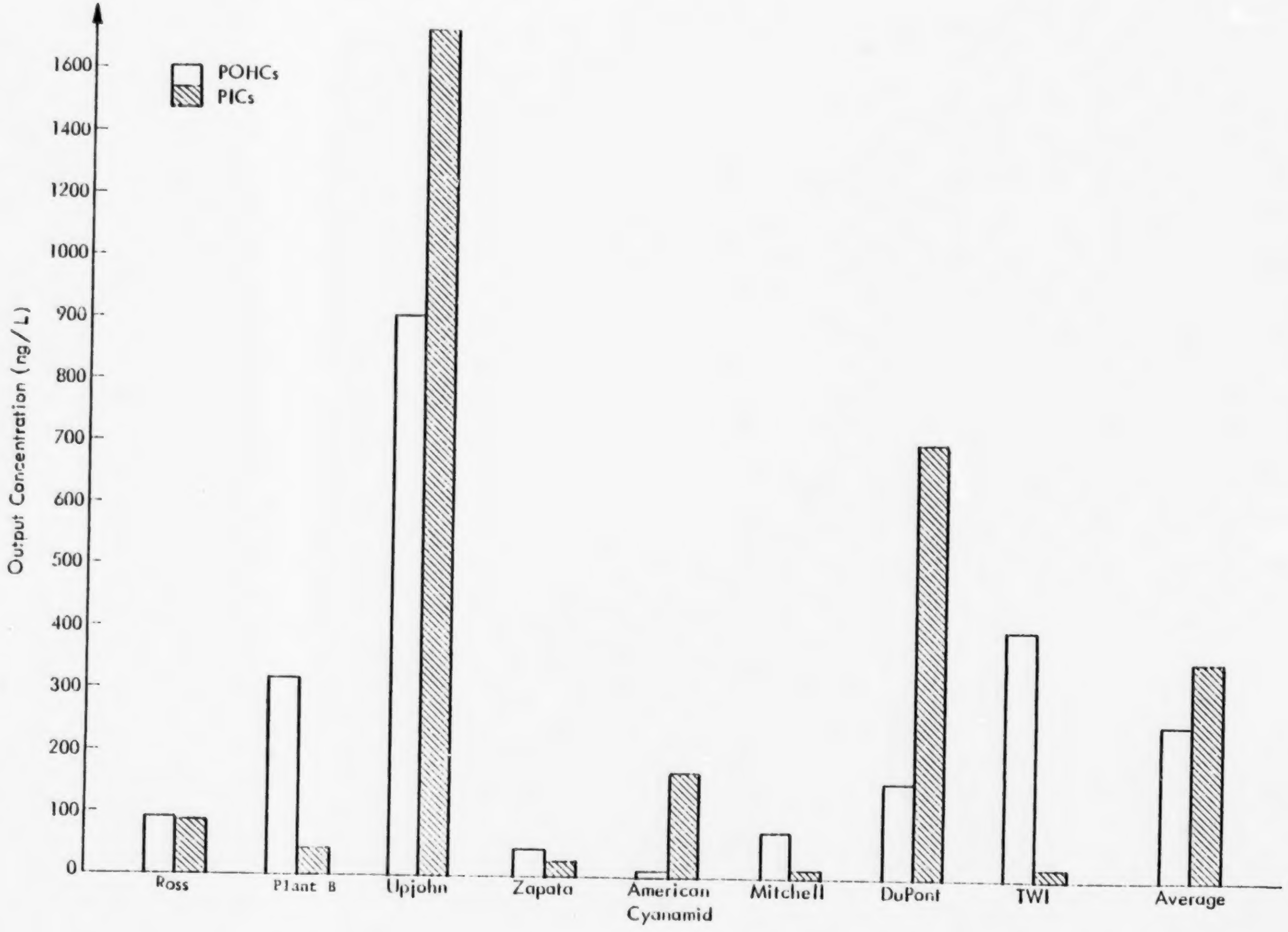


Figure 4-8. Comparison of POHC and PIC concentrations.

TABLE 4-15. CALCULATED VALUES FOR PIC EMISSIONS AS A PERCENT OF POHC INPUT

Calculated values for PIC emissions as a percent of POHC input:

$$\% = \frac{\text{PIC output (g/min)}}{\text{POHC input (g/min)}} \times 100$$

Plant	PIC output (g/min)	POHC input (g/min)	%
Ross	0.090	9,800	0.00092
Plant B[a] (semivolatiles only)	0.0046	100	0.0044
Upjohn	0.092	780	0.012
Zapata	0.00062	27	0.0023
Am Cy	0.011	1,200	0.00091
Mitchell	0.00090	310	0.00029
Du Pont	0.26	8,300	0.0031
TWI	0.0076	1,200	0.00061

[a] High blank values for volatile PICs.

However, other PIC compounds were detected in the stack at all three of these facilities, but were not detected in the waste feeds. This mechanism would not account for those PIC levels. Similarly, some PICs were detected in the stack at levels which would require feed concentrations in excess of 1,000 µg/g and less than 99.9% DRE (e.g., benzene at Du Pont and chloroform at Upjohn); so, it is unlikely that this mechanism would account for those levels. Unfortunately, the detection limits in most waste feed samples were too high (10 µg/g or higher) to ascertain the presence of PIC compounds at low concentrations.

4.1.2.2.2 PICs introduced to the system from some other source--The other sources which were examined are feed water to quench, scrubbers, and particulate removal systems; inleak air; and auxiliary fuel.

The contribution of chloroform to the stack gas due to stripping of scrubber waters was discussed in Section 4.1.1.2.4. In addition to chloroform, other trihalomethanes detected in the stack could be explained by this stripping action. Trihalomethanes were the only PIC compounds which could definitely be accounted for by the scrubber waters.

The presence of Appendix VIII compounds in inleak air was also discussed in Section 4.1.1.2.3. Data from the Du Pont incinerator indicate that some of the PIC compounds detected in the stack gas could be contributed by inleak air. Inleak air could account for up to 10% of the benzene and chlorobenzene detected in the stack. The data are too limited to draw any general conclusions, but inleak air may significantly contribute to low level PIC concentrations in some cases.

Auxiliary fuel was used at four facilities (three used natural gas, one used fuel oil). The fuel oil used at TWI was analyzed and was found to contain 8 of the 10 compounds identified as POHCs. For four of the eight compounds the fuel oil accounted for a significant percentage of the total POHC input with the fuel oil accounting for up to 73% of the total inputs for a specific run. Although this did not directly contribute to the PIC content in the stack, if similar fuel had been used at a facility where the eight compounds were not present in the waste feed, any uncombusted compound detected in the stack would be classified as a PIC.

4.1.2.2.3 PICs as products of combustion reactions--This mechanism is the least understood of the three possibilities because it requires considerable knowledge of the kinetics of reactions occurring in a mixture of chemicals at 2000°F. In spite of the general lack of such information some basic assumptions can be made and tested using the information collected. One assumption is that at these temperatures PICs would consist of fairly stable fragments of compounds in the waste feed, or possible products of simple reactions involving POHCs.

This assumption suggests that benzene, toluene, phenol, and aniline could be detected in the stack gas when aromatics are in high concentrations in the feed. The concentrations of these compounds in the stack were compared with concentrations of aromatics in the feed, and no clear pattern appeared. This analysis is complicated for several reasons: (1) aromatics not on the POHC list would not show up in the waste feed analysis; (2) the reactivity of the simple ring compounds varies greatly among the compounds and is not easily predictable at incinerator conditions; (3) when a compound occurs as a POHC (e.g., benzene) it is impossible to differentiate between unreacted POHCs and newly formed PICs.

In certain special cases the argument for PICs as a product of combustion reactions can be tested. One such case is the Upjohn incinerator where chloroform was detected in high concentrations in the stack. A possible mechanism for the thermal decomposition of phosgene to form chloroform has been examined based on the following reaction:

$$COCl_2 + HCl \rightarrow CHCl_3 + 1/2\ O_2 \text{ (phosgene converted to chloroform)}$$

Thermodynamic equilibrium calculations at combustion chamber temperatures predict chloroform concentrations roughly a million times lower than those detected in the stack. Therefore, the presence of chloroform due to equilibrium reached during the conversion of phosgene due to this, or any other simple reaction involving phosgene and chloroform is not likely. It is possible that chloroform may be an intermediate in some other reaction involving phosgene or any of the other compounds present.

Another similar case is the presence of nitrophenols at both of the plants which burned aniline compounds. Nitrophenol is a likely intermediate in the oxidation process of aniline. Proof of these mechanisms requires the evaluation of the possible reaction kinetics and ensuing equilibria in the environment of the combustion chamber. The data from the tests do not provide enough information to make such complex evaluations.

The occurrence of simple stable compounds such as chlorinated methanes, ethanes, and benzene compounds found in almost all stacks gives support to the hypothesis that some PICs may be formed from simple reactions in the combustion process. Primary candidates for this list on the basis of these tests would include compounds which were present in all stack samples regardless of their presence in the waste feed. These would include: methylene chloride; chloroform; carbon tetrachloride; trichloroethylene; tetrachloroethylene; 1,1,1-trichloroethane; benzene; toluene; chlorobenzene; naphthalene; and phenol. Although this study is inconclusive regarding carbon tetrachloride and trichloroethylene due to their presence in the waste feed at seven of the eight facilities, their presence as PICs is confirmed in studies on the burning of TCE[2] and incineration of chlorinated organics in a cement kiln.[3] Either benzene or toluene accounted for the highest measured stack concentrations of any compound at seven of the eight tests. This occurred regardless of whether the compounds were listed as a POHC or PIC. Certain compounds (e.g., phosgene, formaldehyde) also are suspected of being common reaction products but could not be quantified in these tests due to the sampling and analysis methods used.

To prove the hypothesis that certain compounds are formed as PICs would require analyzing the numerous reactions which could occur with complex mixtures of waste feeds on a plant by plant basis. In addition to differences in waste feed compositions, certain incinerators may have uneven temperature distributions, poor mixing conditions, or low temperature areas which might lead to poor combustion conditions, resulting in an increased likelihood for the formation of PICs. All of these factors would have to be taken into account in the determination of specific mechanisms for the formation of common products of incomplete combustion. Such analyses are beyond the scope of this program.

4.1.2.3 Relative Contribution of PIC Mechanisms--

When the presence of PICs during an incinerator test are examined, it is important to assess the relative contribution of the three mechanisms discussed above. First, nonincinerator sources should be sampled to account for the possibility of compounds contributed by scrubber water (esp. THMs), auxiliary fuel, or inleak air. Second, the feed should be analyzed for low level hazardous constituents whenever possible since a low level POHC (10 µg/g) with a projected DRE of 99.5% (from Figure 4-1) could potentially contribute as much to stack concentration and total mass output as a high level POHC (10,000 µg/g) with a projected DRE of 99.9995%. Any compound not accounted for by the above two mechanisms may be a true PIC (i.e., formed in the combustion process).

Figure 4-9 summarizes the relative potential contribution of each of these mechanisms to the total mass output of PICs. Low concentration POHCs in the waste feed potentially accounted for 0 to 68% of the total mass of PICs detected at each facility. The higher percentages were for the plants with the lowest total mass of PICs. The stripping of trihalomethanes from the waters potentially accounted for up to 14% of the total mass of PICs detected. The rest of the compounds were most likely actual products of combustion reactions. Figure 4-9 also includes a bar which represents the percent of the PICs which fall into the following list of most common compounds (MC):

Compound	Concentration Range (µg/L)	Number of Plants as a PIC
Chloroform	1.5 - 1,330	5
Benzene	13 - 670	6
Naphthalene	4 - 120	3
O-nitrophenol	25 - 35	2
Bromoform	0.21 - 23	3
Phenol	5 - 19	2

This list is based on both frequency of occurrence as a PIC and concentration. As can be seen from Figure 4-9, this brief list accounts for a substantial percentage of the total PIC output at many facilities.

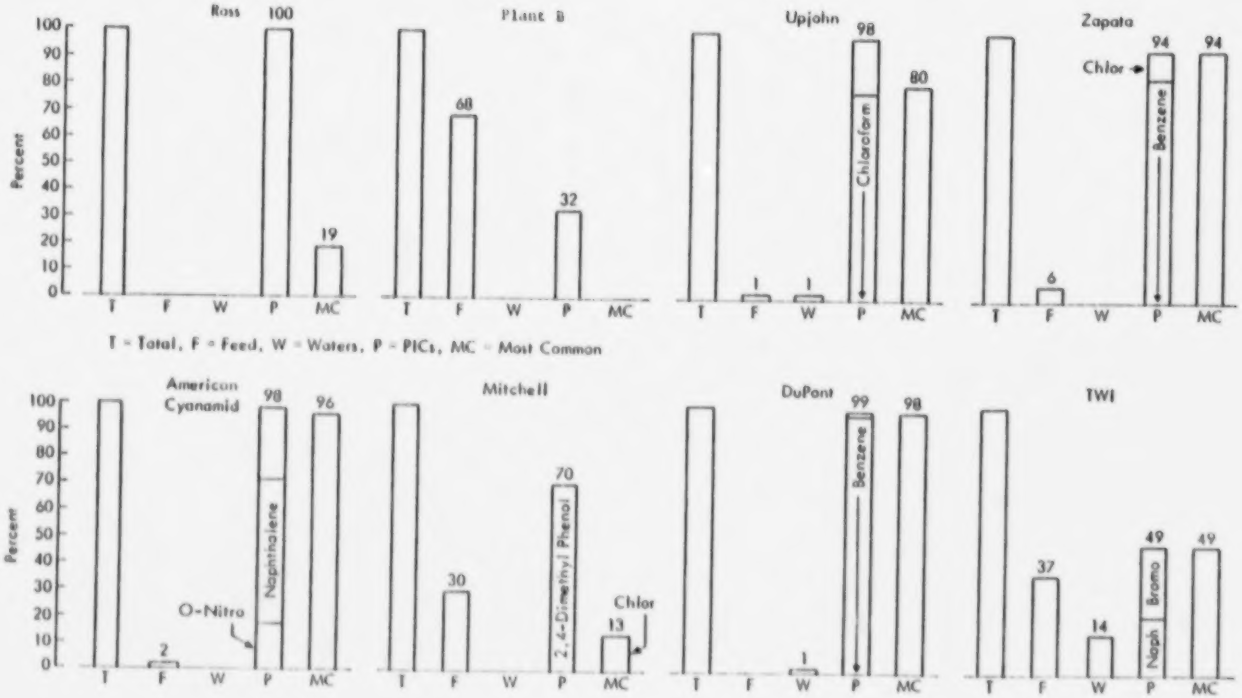


Figure 4-9. Percentage of PICs attributed to different mechanisms.

4.1.2.4 Dioxins and Furans Detected in Stack Samples--

Samples of stack emissions from six facilities (Plant B, Upjohn, Mitchell, Ross, American Cyanamid, and Du Pont) were analyzed for tetrachlorodibenzofurans (TCDF), pentachlorodibenzofurans (PCDF), tetrachlorodibenzodioxins (TCDD), and pentachlorodibenzodioxins (PCDD). Furans were detected at three of the six facilities (Plant B, Upjohn, and Mitchell), but dioxins were found at only one facility (Plant B). Detection limits ranged from 0.0003 to 0.002 ng/L. The concentration ranges in the stack samples were:

TCDF: 0.0007-0.047 ng/L
PCDF: 0.0005-0.023 ng/L
TCDD: 0.021 ng/L
PCDD; 0.001 ng/L

Table 4-16 shows these results in more detail. These results are within the ranges reported in the literature for emissions from municipal refuse incinerators.[4]

Three TCDD isomers were identified at Plant B: 1,2,6,8-TCDD; 1,2,3,6- or 1,2,7,8-TCDD; and 1,3,6,8- or 1,2,4,7- or 1,2,4,8-TCDD. No 2,3,7,8-TCDD was detected.

The results were in agreement with previous conclusions in the literature that the concentration of dioxins in the vapor phase of a flue gas sample exceeds the concentration of dioxin in the particulate.[5] The data indicate 71 to 100% of the dioxin detected was present as a gas when collected by the sampling train. A comparison of inlet and outlet sample results at Plant B shows lower values for furan concentrations for the outlet sample. PCDD and TCDD were about the same in the inlet and outlet samples. Due to the extremely low concentrations involved and the limited number of samples analyzed, any conclusions reached relative to removal by the control system would be tentative.

The waste feeds for the six facilities were reviewed for possible precursors of dioxins and furans. Table 4-17 presents the results of this review. The three plants with detectable quantities of furans or dioxins in the stack gas also had the most benzenes and/or phenols (possible precursors) in the waste. This apparent association is only suggestive because the data base is quite limited, and the formation of dioxins and furans is probably also dependent on other incinerator parameters not examined.

4.1.3. Continuous Monitoring Data as Indicators of Incinerator/Performance

The DRE values obtained during a trial burn measure incinerator performance only over a short time span under a specified set of conditions. They do not necessarily reflect the long-term or continuing performance of the incinerator. One suggested method for monitoring long-term performance is to use continuous stack monitors, particularly CO and THC monitors, as indicators of continuing incinerator performance.

TABLE 4-16. RESULTS OF ANALYSIS OF STACK SAMPLES

	Back half only[a] (ng/L)					
	Ross	Plant B	Upjohn	American Cyanamid	Mitchell	Du Pont
Tetrachlorodibenzofurans	< 0.0001	0.040	0.0068	< 0.0001	0.0007	< 0.0001
Pentachlorodibenzofurans	< 0.0001	0.016	0.0005	< 0.0001	0.0010	< 0.0001
Tetrachlorodibenzodioxins	< 0.0001	0.015[b]	< 0.0001	< 0.0001	< 0.0001	< 0.0001
Pentachlorodibenzodioxins	< 0.0001	0.001	< 0.0001	< 0.0001	< 0.0001	< 0.0001

	Selected samples front half and back half[a] (ng/L)								
	Plant B inlet			Plant B stack			Mitchell stack		
	Front half	Back half	Total	Front half	Back half	Total	Front half	Back half	Total
Tetrachlorodibenzofurans	< 0.0009	0.086	0.086	0.0074	0.040	0.047	< 0.0002	0.0007	0.0007-0.0009
Pentachlorodibenzofurans	< 0.0009	0.086	0.086	0.0068	0.016	0.023	< 0.0002	0.0010	0.0010-0.0012
Tetrachlorodibenzodioxins	< 0.0009	0.020[b]	0.020[b]	0.0063[b]	0.015[b]	0.021[b]	< 0.0002	< 0.0001	< 0.0003
Pentachlorodibenzodioxins	< 0.0009	< 0.0002	< 0.0011	< 0.001	0.001	< 0.002	< 0.0002	< 0.0001	< 0.0003

---

[a] Back half refers to condensate and XAD resin samples in the MM5 sampling train. Front half refers to filter and probe rinse samples in the MM5 sampling train.

[b] Three TCDD isomers were identified as follows: 1,2,6,8-TCDD
1,2,3,6- or 1,2,7,8-TCDD
1,3,6,8- or 1,2,4,7- or 1,2,4,8-TCDD

TABLE 4-17. POSSIBLE PRECURSORS TO DIOXINS AND FURANS

Plant	Detected in stack		POHCs in waste				PICs in stack	
			Benzenes		Phenols			
	Dioxins	Furans	Compound	Concentration (μg/g)	Compound	Concentration (μg/g)	Benzenes	Phenols
Plant B	yes	yes	none	---	phenol	1,700	dichlorobenzene trichlorobenzene hexachlorobenzene benzene	none
Upjohn	no	yes	chlorobenzene dichlorobenzene trichlorobenzene	800 20,000 60	none	---	hexachlorobenzene benzene	chlorophenol trichlorophenol hexachlorophenol phenol
Mitchell	no	yes	benzene	120	phenol	19,000	chlorobenzene	none
Ross	no	no	none	---	phenol	60	benzene	none
American Cyanamid	no	no	none	---	none	---	chlorobenzene benzene	none
DuPont	no	no	none	---	none	---	chlorobenzene benzene	phenol

As a part of this program, CO and THC were monitored continuously during the VOST and MM5 testing at each of the eight test sites. The CO and THC data were subsequently reduced and compared to both POHC concentrations and DREs. This section reports the results from those analyses. The first subsection below describes the CO and THC data base. The second and third subsections describe the relationships of both CO and THC to POHC concentrations and DREs respectively.

4.1.3.1. Summary of CO and THC Data--

CO and THC stack emissions were monitored continuously during testing at each of the eight sites. The CO emissions were measured by a nondispersive infrared detector (NDIR), and THC emissions were measured using a flame ionization detector (FID). Both of these methods are described in Appendix B. The data from the continuous monitors were reduced to a series of 1 min averages using a microprocessor. The 1 min averages were subsequently reduced to a 20-min average and run averages for the analyses described in this section. Table 4-18 summarizes these data for both CO and THC. The table includes the range of concentrations (based on 1 min averages) and the average run concentration for each run at each test site. The 20-min averages that were used for some analyses are presented in Table 4-19.

The key factor regarding these data is that most of the observations are quite low. Experienced field personnel indicate that the continuous monitors can accurately quantify CO at levels above about 5 ppm and THC at levels above about 2 ppm. Review of the data indicate that almost all of the run averages were at or near these quantitation magnitudes. The five notable exceptions were Run 5 at Plant B, a run in which operating conditions were set to produce poor combustion; Run 1 at Zapata, a run in which the probes were placed in a section of the stack where combustion flame was still present; and all three runs at Du Pont. Some of the high spikes for CO and THC at Du Pont appear to be associated with charging of paint cans to the kiln. However, no cause for the high baseline levels of CO and THC was identified.

4.1.3.2 Comparison of CO and THC Concentrations to POHC/PIC Concentrations--

In order to evaluate the suitability of continuous CO and/or THC measurements as surrogates for hazardous organic emissions, analyses of the relationships between CO and THC concentrations and concentrations of specific organic constituents in the stack gases were conducted. These analyses suggest that CO or THC concentrations may provide some indicator of changes in incineration performance but for the plants tested they did not appear to be good predictors of hazardous organic stack concentrations either across plants or at a specific site. The paragraphs below provide a more detailed discussion of analytical methods and results. The initial paragraphs describe a nonparametric analysis of the bivariate relationships between CO and THC concentrations and concentrations of some of the more common POHCs. Later paragraphs describe the results of multivariate parametric analyses.

TABLE 4-18. SUMMARY OF CONTINUOUS MONITORING DATA

Plant	Run No.	CO (ppm_v) Range	CO (ppm_v) Average	THC (ppm_v) Range	THC (ppm_v) Average
Plant B	1	10.6-22.5	14.8	< 1	< 1
	2	< 1	< 1	< 1	< 1
	3	1.6-10.7	6.9	< 1.0-1.9	< 1
	4	5.9- 8.4	7.2	< 1.0-1.1	< 1
	5	3,513-5,400	4,300	266-523	341
Ross	1	2.1- 7.4	4.8	< 1	< 1
	2	4.7-15.5	9.1	0.8- 2.3	0.9
	3	2.9- 8.7	4.7	< 1- 2.3	1.0
Upjohn	1	10.3-11.0	10.5	7.1-11.9	8.9
	2	10.7-11.4	11.2	4.5- 9.0	6.0
	3	9.3-10.0	9.9	3.1- 6.2	3.9
Zapata	1	739-1,570	1,275	32-215	71
	2	< 1 - 394	22.2	< 1-40.9	1.9
	3	3.6- 8.8	7.5	< 1	< 1
	4	2.8-18.3	8.8	< 1- 2.9	< 1
American Cyanamid	1	1.2-30.7	6.7	< 1 - 1.6	< 1
	2	8.3-37.3	19.3	< 1- 2.6	< 1
	3	-	-	< 1- 1.2	< 1
	4	7.0-25.5	13.8	< 1	< 1
	5	8.6-25.7	14.3	< 1- 1.1	1.0
Mitchell	1	0 - 4.6	1.4	< 1	< 1
	2	0.2- 3.0	1.8	< 1	< 1
	3	0 -12.7	< 1	0.2- 1.8	0.6
Du Pont	1	34-1,150	666	45.0-140	75.9
	2	34-1,510	422	36.2-85.8	47.6
	3	60-1,510	624	39.4-86.3	58.1
TWI	1	1.2-66.3	4.3	2.0- 2.9	2.5
	2	0 -13.8	0.9	1.7- 2.1	1.9
	3	0 - 2.3	1.2	1.3- 2.2	1.7
	4	0 - 2.0	0.6	0.3- 2.1	0.8

TABLE 4-19. TWENTY MINUTE AVERAGE CONTINUOUS MONITORING DATA

Plant[a]	Run segment[b]	CO (ppm_v)	THC (ppm_v)	Plant	Run segment	CO (ppm_v)	THC (ppm_v)
Zapata	2-1	66.5	8.6	Du Pont	1-1	724.6	90.5
	2-3	5.4	0.2		1-3	614.7	85.1
	2-6	4.1	0		1-6	597.7	86.1
	3-1	4.2	0		2-1	66.5	42.1
	3-3	4.0	0		2-3	128.4	42.2
	3-6	5.4	0		2-6	537.3	62.8
					3-1	222.2	61.6
American Cyanamid	1-1	2.6	0.8		3-3	590.2	57.9
	1-2	2.1	0		3-6	677.1	61.3
	1-3	2.8	0				
	2-1	97.0	0.5	TWI	1-1	3.5	2.7
	2-2	8.0	0.1		1-3	2.3	2.5
	2-3	4.0	0.1		1-5	2.6	2.4
	3-1	14.6	0.4		1-6	2.3	2.4
	3-2	14.6	0.2		2-1	0.9	2.1
	3-3	14.6	0.1		2-3	0.8	1.9
	4-1	17.2	1.0		2-5	0.7	1.8
	4-2	6.4	0.9		2-6	0.4	1.8
					3-1	0.7	2.1
Mitchell	1-1	0.1	0		3-3	0.8	1.8
	1-3	1.3	0		3-5	1.3	1.5
	1-6	3.8	0		3-6	1.5	1.6
	2-1	1.6	0		4-2	0.4	0.7
	2-3	1.8	0		4-4	1.2	0.7
	2-6	0.7	0		4-5	1.2	0.5
	3-1	18.3	0		4-6	0	0.5
	3-3	1.5	0				
	3-6	3.3	0.1				

[a] Twenty minute average data were calculated only for the last five sites because corresponding organic data for the first three sites was of limited quality due to blank problems.

[b] Each run lasted 2 hrs with six 20 min segments in each run. These segments correspond to the VOST traps that were subsequently analyzed.

Two nonparametric methods--rank order correlation (Spearman) and a distribution free rank sum test (Wilcoxon), were used to investigate potential relationships between CO/THC and POHC/PIC emissions. These methods provide information similar to that yielded by more familiar parametric methods--Pearson's correlation coefficient (r) and the two sample t-test, respectively. The principal advantage of nonparametric over parametric methods is that they depend only on relative ranks and thus should be less sensitive to uncertainties in the actual magnitudes of the observations. Other advantages of nonparametric methods are that they do not require normally distributed data, nor do they require that bivariate relationships be linear.

The analyses considered data from the last four tests because the organics data from those tests were considered to be most reliable. Attention was restricted to concentrations (ng/L) of four compounds--benzene, toluene, carbon tetrachloride, and trichloroethylene. These compounds were selected because they represent a wide range in types of compounds and heats of combustion and because they were present at most test sites. The basic analysis units are measurements obtained from the fast VOST pairs and the corresponding time-averaged CO/THC measurements.

The key parameter from the rank sum test, Δ, is a measure of the difference of the median POHC concentrations for the detectable and nondetectable CO/THC populations. Estimates of Δ and 90% confidence limits (shown in parentheses) are presented in Table 4-20. Three of the eight cases in Table 4-20 show significant shifts in location. All three significant shifts are associated with THC while, two of the four Δ's for CO/compound tests are negative, implying at least some tendency toward higher levels of toluene and TCE in the absence of detectable CO. These conclusions should be viewed with caution in that they are based on the assumption that the two groups are dispersed in a similar manner. For benzene, this assumption may have been violated, leading to the wide confidence level.

TABLE 4-20. ESTIMATES OF SHIFT IN LOCATION (Δ)[a]

	Benzene	Toluene	Carbon-tetrachloride (CCl_4)	Trichloroethylene (TCE)
CO	2.3 (-6.1, 31)	-19 (-140, 0.5)	0.90 (0.11, 2.1)	-1.6 (-3.9, -0.5)
THC	70 (7.5, 104)[b]	11 (0.5, 25)[b]	2.0 (0.8, 4.0)[b]	-0.05 (-1.4, 2.1)

[a] Measured in units of ng/L.

[b] Significant at the 10% level, i.e., Δ's of this magnitude would be obtained by chance only 10% of the time.

The results from the rank order analysis presented in Table 4-21 indicate that in four of the eight cases the relationship may be considered significant. Three of the four significant relationships are between CO and the compounds (benzene, toluene, and CCl_4) implying that increases in CO concentrations above detection limits are a more effective indicator of increases in POHC/PIC emissions concentrations than are the corresponding THC concentration increases.

TABLE 4-21. RANK ORDER CORRELATIONS (r_{sp})

	Benzene	Toluene	Carbon-tetrachloride	Trichloroethylene
CO	0.80[a]	0.79[a]	0.51[a]	0.006
THC	0.42[a]	-0.20	0.053	-0.55

[a] Significant at the 10% level; i.e., correlations of this magnitude would be obtained by chance only 10% of the time.

When taken together these results suggest that increases in CO concentrations may also indicate increases in concentrations of specific organic constituents in the stack gases. However, high concentrations of organic constituents in the stack gas can occur concurrently with low CO concentrations. Hence, CO monitors may be useful but are not good predictors of hazardous organic constituent stack gas concentrations. These results are illustrated in Figures 4-10 and 4-11 which graph the relationships between CO and benzene and carbon tetrachloride, respectively. In both graphs positive variation between CO and the organic constituent can be noted when the CO levels are above 5 ppm. However, high organic concentrations were present in some cases when CO was not detected.

The results described above were confirmed by subsequent multivariate analyses. Principal component analysis was conducted using the data from the last five tests for six compounds - benzene, toluene, trichloroethylene, carbon tetrachloride, methylene chloride, and tetrachloroethylene. The objective of the principal component analysis is to identify the key variables that had the greatest impact on the variation among the test observations. As an intermediate product, the method produces correlation coefficients (r) for all input variable pairs. This matrix showed no correlation between CO or THC and stack concentration of organic constituents.

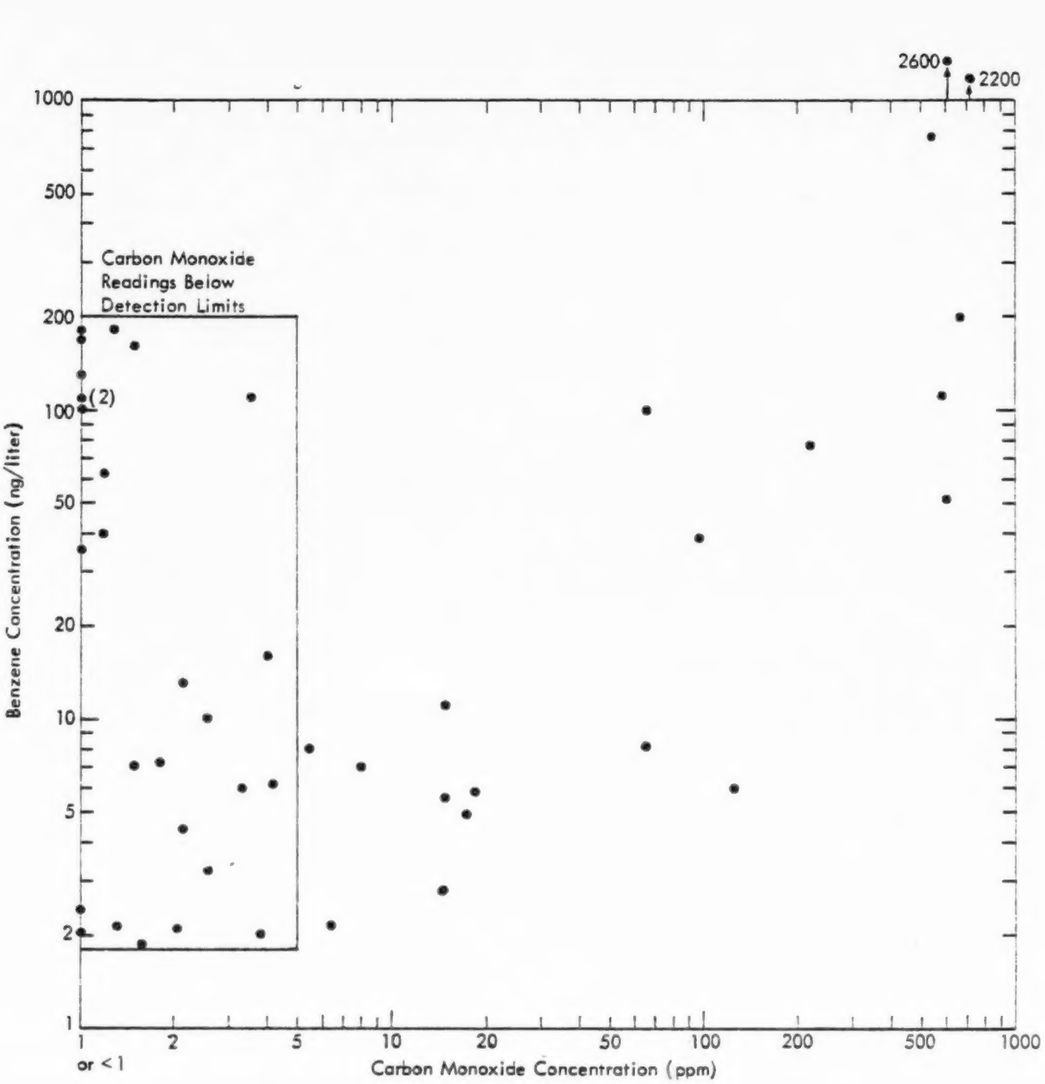


Figure 4-10. Benzene concentration versus CO concentration.

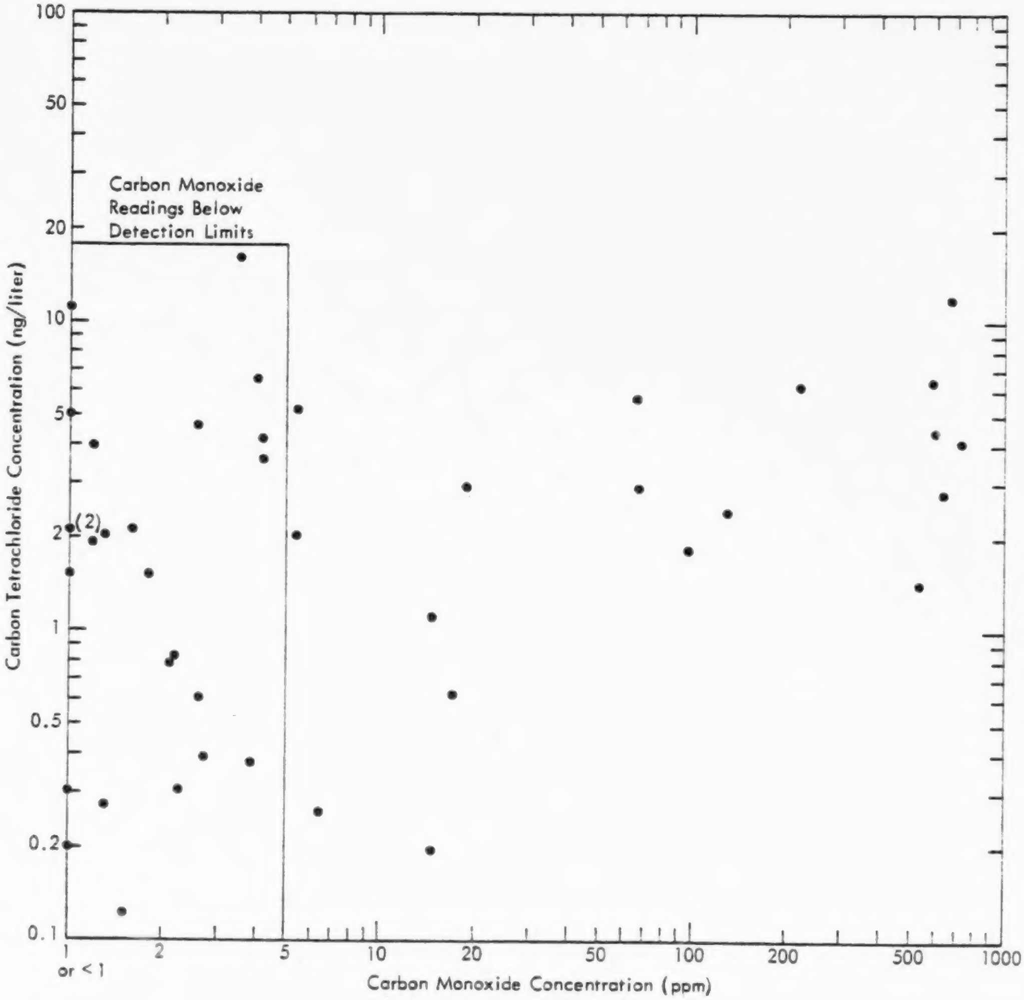


Figure 4-11. Carbon tetrachloride concentration versus CO concentration.

4.1.3.3 Comparison of CO Concentrations to DRE--

As an extension of the analyses described in the previous section, the relationship between CO concentrations and DRE was also examined. Both nonparametric and parametric methods were used. These results suggest that CO may provide some indications of changes in incinerator performance but that they are not a good predictor of DRE, either at a specific plant, or across plants.

The analysis compared the average CO concentration for a run to the penetration (1-DRE) of a specific POHC for the same run using the data for carbon tetrachloride, toluene, trichloroethylene, and tetrachloroethylene. If CO is to be useful as a predictor of DRE, these two variables should exhibit a positive rank correlation coefficient (r_{sp}) which indicates a positive monotonic relationship. However, when all data points were used in the analysis, r_{sp} was negative for each of the four POHCs as shown in the second column in Table 4-22. Each of the rank correlation coefficients was significant.

Examination of these results indicated that they were strongly influenced by the three data points from Du Pont, the site which consistently had the highest CO concentrations and lowest penetrations. Each r_{sp} was then calculated with the Du Pont data omitted. The resulting coefficients were still negative, as shown in the third column of Table 4-22, but none of these results was significant. With Du Pont data omitted, the correlation between CO concentration and penetration was not determined to be significantly different from 0, i.e., no relationship could be established.

TABLE 4-22. RANK ORDER CORRELATIONS (r_{sp})

Compound	All observations	Du Pont observations omitted
Carbon tetrachloride	-0.61*	-0.18
Trichloroethylene	-0.55*	-0.27
Toluene	-0.74*	-0.43
Tetrachloroethylene	-0.59*	-0.083

* Significant at the 5% level, i.e. correlation coefficients of this magnitude would be obtained by chance only 5% of the time.

These results were confirmed by the principal component analysis described in Section 4.1.3.2. The correlation matrix showed no significant correlation between CO concentration and DRE. Further, a discriminant analysis used to identify the parameters that discriminated between those observations that achieved 99.99% DRE and those that failed did not identify CO concentration as an important parameter.

The results discussed in the preceding paragraph should be viewed with caution in that they are based on CO data which for the most part are at or near detection limits. They may not hold in cases where higher CO levels are obtained. In this regard two interesting observations from the Du Pont data are worth noting:

- At Du Pont CO concentrations were lower for Run 2 (about 250 ppm) than for Runs 1 and 3 (about 500 ppm). Run 2 also had the highest DRE for all compounds that were above detection limit.
- Du Pont, with the highest levels of CO by more than an order of magnitude, achieved 99.99% DRE for all volatile POHCs and all semivolatile POHCs except naphthalene. No other plant achieved 99.99% DRE on all volatile POHCs.

In conclusion, CO may be an indicator of changing performance, but it does not appear to be valuable in predicting absolute performance.

4.2 CONTROL OF HYDROGEN CHLORIDE AND PARTICULATE EMISSIONS

Although the major concerns related to hazardous waste incinerator emissions have focused on organic constituents in the exhaust gases (i.e., DRE), chloride emissions and particulate emissions (including metals emissions), are also of concern. These emissions are covered by current hazardous waste incinerator regulations. HCl emissions are limited to the greater of 1.8 kg/hr (4 lb/hr) of HCl or 1% of the total organic chloride in the waste. The maximum allowable particulate concentration is 180 mg/Nm^3 (0.08 gr/dscf) as corrected to 7% O_2.

Add-on air pollution control devices are frequently used to achieve compliance with the regulations, because control of HCl and particulate emissions is not inherent to combustion. Generally one or more absorption scrubbers are used for HCl control. Particulate control is often achieved by venturi wet scrubbers or ionizing wet scrubbers (a type of electrostatic control device). As outlined in Section 3, five of the eight incinerators tested during this study had some type of absorption scrubber for HCl control. For particulate control, two facilities had venturi scrubbers, one had an ionizing wet scrubber, and one had a novel device--an electrified gravel bed filter.

One of the objectives of the study was to evaluate the performance of these HCl and particulate control systems. The degree to which this objective could be addressed was limited by the constraints placed on sampling activities by the facility designs. Only one of the eight facilities had control device inlet sampling locations suitable for testing. As a result, the analysis of control device performance described in this section is based principally on outlet sampling.

The remainder of the section presents available data on control device performance in three subsections. The first describes the HCl control systems sampled and analyzes the performance of those systems. The second subsection addresses particulate emissions. The final subsection presents the available data on metals emissions and analyzes the performance of the particulate control systems with respect to metals control.

4.2.1 Control of HCl Emissions

Chloride emissions, principally in the form of hydrogen chloride (HCl), are generated from the combustion of chlorinated compounds in hazardous waste incinerators. The three principal measures used to control HCl emissions are: (a) to limit the chlorine content of the waste feed with no add-on control; (b) to use an absorption scrubbing system with water as the absorbing medium; and (c) to use a caustic absorption scrubbing system. Each of these three types of systems was encountered during this study. The two subsections below describe the control systems tested and compare the performance of the alternate systems.

4.2.1.1 Description of HCl Control Systems--

Essentially all hazardous waste incinerators that require add-on HCl control equipment use some type of countercurrent flow wet scrubber to remove HCl from the exhaust stream. Since HCl is highly soluble in water, an aqueous scrubbing liquid is generally used. The basic control mechanism is absorption of the gaseous HCl into the liquid.

Although this mechanism is common, a variety of scrubber designs are used. Some scrubbers use water as the scrubbing liquid, while others use a caustic solution. With either liquid, the flow may be once through or recirculated. A variety of designs are used to provide large liquid surface areas, including spray towers, packed towers, and different tray arrangements. In some cases the system contains a single scrubber, but other systems have multiple scrubbers in series. Although HCl scrubber systems exhibit a variety of design and operating conditions, control efficiency is primarily affected by five key parameters: (a) the HCl concentration of the entering gas stream; (b) the concentration of Cl^- ions in the scrubber influent and effluent streams; (c) the superficial gas velocity through the scrubber; (d) the liquid/gas ratio; and (e) the number of scrubber transfer units, a function of tower height and configuration.

As indicated in Section 3.3, five of the eight incinerators tested during this program had HCl control systems. These systems were described briefly in Section 3.3, and more detailed descriptions are included in Appendices C through J. Table 4-23 presents key operating parameters for four of these five control systems. The data in the table show the wide range of operating conditions represented by the facilities tested. Two of the systems shown had single-stage scrubbing systems, while two had multiple-stage systems. Two of the systems used water only as a scrubbing liquid, while two added caustic for pH control. Both the liquid/gas ratios and superficial gas velocities vary over a wide range. The liquid gas ratios range from 7.2 to 23.9 L/Nm^3 (54 to 180 gal/1,000 scf). All values appear to be conservatively high, based on typical design values. The superficial

TABLE 4-23. KEY PARAMETERS FOR HCl CONTROL SYSTEMS

Facility	Configuration	Scrubbing liquid	Cl⁻ concentrations: Scrubber liquids (g/L) Influent	Cl⁻ concentrations: Scrubber liquids (g/L) Effluent	Cl⁻ concentrations: Stack gas (mg/Nm³) Inlet	Cl⁻ concentrations: Stack gas (mg/Nm³) Outlet	pH Scrubber influent	pH Scrubber effluent	Liquid/gas ratio (L/Nm³)	Packing depth (m)	Superficial gas velocity (m/sec)
Ross											
1st absorber	Packed tower	Caustic	17.3	18.4					23.9		
2nd absorber	Packed tower	Caustic				2.3		7.80	7.2		
Upjohn	Packed tower	Water	21.1	23.9		180		< 1	11.4	4.3	0.31
Du Pont											
1st absorber	Disc/doughnut	Water		40.5[a]				1		(4)[b]	0.85
2nd absorber	Packed tower	Water								3.7	1.26
3rd absorber	Packed tower	Water	0.014[a]			14.2				3.7	1.26
TWI	Venturi/mist eliminator	Caustic				19.6	10.2	9.4		NA	

[a] Scrubber makeup enters the 3rd scrubber and is recirculated through the system. All blowdown is taken from the first scrubber.

[b] Number of trays in the system, not the depth.

gas velocities range from 0.31 to 1.26 m/sec (61 to 250 ft/min). These values appear to be at the low (conservative) end of typical design values for packed bed scrubbers.

4.2.1.2 Performance of Alternate Systems--

As indicated earlier, the eight plants tested during this study comprised three control scenarios--no HCl control, control with water only absorption, and control with caustic aqueous absorption. This section discusses the performance of these alternate systems in two subsections. The first describes HCl emissions from the three uncontrolled sites. The second evaluates the performance of the HCl control systems at the five sites tested during this program.

4.2.1.2.1 HCl emissions from uncontrolled incinerators--Emissions data are available for three facilities--Zapata, American Cyanamid, and Mitchell--which had no HCl control. (These sites contained no controls because low chloride wastes are fired under normal operating conditions.) Inlet sampling prior to the wet scrubber at Plant B provides additional data on uncontrolled HCl emissions. The chloride feed rates and uncontrolled emission rates for these four sites are presented in Table 4-24.

Both Zapata and American Cyanamid complied with the HCl emission standard of 1.8 kg/hr. Since most of the chlorides in the Mitchell waste were a result of spiking, the system would easily have complied with the standard under normal operating conditions.

One interesting result apparent in the table is the wide range of chloride emissions as a function of chloride input. At Zapata and Plant B, essentially all of the chlorides that were in the feed were also detected in the stack gases. However, both American Cyanamid and Mitchell had much lower fractions of the chlorides in waste feed present in the stack gas. Mitchell emitted about 50% of the feed chlorides through the stack, and American Cyanamid emitted only about 10%. The results at American Cyanamid can possibly be explained by measurement errors due to the small quantities present in both the waste feed and stack gas. However, no apparent reason for the differences at Mitchell could be identified.

4.2.1.2.2 Performance of the HCl control systems tested--This section presents the available data on the performance of the five different HCl control systems tested during this program. Complete characterization of the performance of the systems is complicated by the fact that: (a) inlet gas samples were only taken at one site--Plant B; (b) the variation in emissions as a function of feed rates at the uncontrolled sites makes estimation of inlet emissions as a function of waste feed rates impossible; and (c) data on scrubber water flow rates and chloride concentrations are incomplete. As a result, discrete observations concerning scrubber performance are discussed, rather than a comprehensive evaluation of scrubber potential.

Available data on chloride input rates, stack emission rates, and chloride catch in the scrubber are presented in Table 4-25. The data in

TABLE 4-24. SUMMARY OF HCl EMISSIONS DATA FROM FACILITIES WITH NO CONTROL

Site	Run No.	Chloride feed rate (kg/hr)	Emission rate (kg/hr)	Emission rate / Feed rate
Plant B (Inlet)	1	54.7	59.5	1.09
	2	69.8	73.7	1.06
	3	50.8	63.2	1.24
Zapata	1	1.07	1.01	0.94
	2	0.74[a]	0.63	0.85
	3	0.63[a]	1.25	1.98
	4	0.34[a]	1.50	4.41
Mitchell	1	3.76	1.87	0.50
	2	4.27	2.23	0.52
	3	3.07		
	4	4.30	1.73	0.40
American Cyanamid	1	0.026	0.004	0.15
	2	0.015	0.002	0.13
	3	0.027	0.003	0.11
	4	0.025	0.003	0.12
	5	0.025	0.003	0.12

[a] Values suspect due to nonrepresentative waste samples.

TABLE 4-25. SUMMARY OF HCl EMISSIONS FROM FACILITIES WITH CONTROL SYSTEMS

Plant	Run No.	Cl^- waste feed rate (kg/hr)	Cl^- emission rate (kg/hr)	Control efficiency (%)	Cl^- in scrubber effluent (kg/hr)
Ross	1	214	0.0678	99.968	
	2	197	0.134	99.932	
	3	167	0.132	99.921	
Plant B	1	54.7	0.29	99.5	66.6[a]
	2	69.8	0.83	98.8	84.2[a]
	3	50.8	2.03	96.0	70.9[a]
Upjohn	1	195	0.42	99.79	102
	2	274	0.53	99.81	98.8
	3	218	0.78	99.64	106
Du Pont	1	287	0.235	99.99	242
	2	290	0.295	99.90	302
	3	305	0.407	99.87	339
TWI	1	7.8	0.135	98.3	
	2	10.2	0.161	98.4	
	3	7.8	0.251	96.8	
	4	15.6	0.0978	99.4	

[a] Based on approximate effluent discharge rate of 600 L/min.

Table 4-25 indicate that three facilities--Ross, Upjohn, and Du Pont--consistently achieved greater than 99% HCl removal. In fact, both Ross and Du Pont consistently achieved 99.9% control. Since both facilities had multiple scrubbers in series, this high level of control is expected. However, Upjohn achieved nearly the same level of control with only a single absorber tower.

The Plant B facility achieved 99% HCl control on only one of the three tests, which is not expected based on the design calculations presented earlier. No specific explanation for the reduced performance was identified. However, it was noted that the recirculated water flow rate did decrease through the tests from 726 L/min on Run 1 to 510 L/min on Run 2 to 416 L/min on Run 3. While these liquid flow rates reduce the liquid/gas ratio to lower levels than the other facilities tested, the ratio is still within normal design ranges.

The TWI facility consistently achieved less than 99% HCl control. Since the control system includes a venturi scrubber and mist eliminator intended primarily for particulate control, the inability to achieve 99% HCl control is not surprising. However, the facility did emit less than 1.8 kg of HCl/hr and therefore, met the HCl standard.

The data presented in the last column of Table 4-25 are also of interest. The scrubber liquid effluent at Plant B and Du Pont accounted for essentially all of the chloride present in the waste feed, but the effluent at Upjohn accounted for only about 50%. These data parallel the observations from the uncontrolled facilities on the fraction of the chloride feed that are emitted with the stack gas.

4.2.2 Particulate Emissions Control

The principal sources of particulate emissions from hazardous waste incinerators are the waste feed, auxiliary fuels, and scrubbing liquids used in the air pollution control system. During the combustion process ash from the waste feed or auxiliary fuel can be entrained in the combustion gas exhaust and emitted as particulate. Carbonaceous material can also be entrained in the exhaust gases, condensed in the air pollution control systems, and subsequently emitted to the atmosphere. Suspended and dissolved solids in water used in the air pollution control system are another potential source of particulate emissions. If water droplets are evaporated in a quench chamber or scrubber, solids contained in these droplets can be entrained in the exhaust stream as particulates. Droplet carryover from the control system can also be a source of particulate emissions. As the droplets enter the particulate sampling train, they are evaporated, and any solids contained in the droplets will be measured as particulate.

A variety of control techniques have been used to control particulate emissions from hazardous waste incinerators. The most common techniques include venturi scrubbers and ionizing wet scrubbers. Five of the eight facilities tested during this program had some type of particulate control. Two had high energy wet scrubbers, one had a low energy wet scrubber (which provides minimal control), and one had an ionizing wet scrubber.

The data collected at the five controlled sites suggest that achieving the particulate emissions limitation of 180 mg/Nm^3 (corrected to 7% O_2) may be more difficult than achieving the HCl and DRE standards. This section presents the data that form the basis for this observation and describes some of the potential problems related to particulate control. The section is divided into two parts. The first briefly describes the control systems at the five sites. The second section presents the particulate emissions data and describes the performance of the systems based on the evaluation of those data.

4.2.2.1 Description of the Particulate Control Systems--

This section describes four of the five particulate control systems that were encountered during this program. The paragraphs below present brief physical descriptions of the systems, identify key operating parameters that affect performance, and summarize available data on these parameters.

The Ross incinerator uses a two-stage ionizing wet scrubber (IWS) for particulate control. This scrubbing system relies on a combination of electrostatic and impaction mechanisms to achieve high efficiency particulate control over a wide range of particle sizes. The dirty gas stream enters the ionizing section of the scrubber comprising discharge electrodes of negative polarity and wetted plates which act as positively charged grounds. The particles receive a negative charge in the ionizing section. Particles are removed from the gas stream in the packed scrubber section containing wetted plastic Tellerette packing. Larger particles are removed by impaction, and smaller particles (< 3 µm) are attracted to the neutral surfaces electrostatically. The particles are washed from the packing by a constant water flow. The key parameters for particulate control are the field strength in the ionizing section, the superficial gas velocity in the scrubbing section, and the packing depth. The measurements of these parameters taken during the test are summarized in Table 4-26.

TABLE 4-26. OPERATING PARAMETERS FOR ROSS IONIZING WET SCRUBBERS

Parameter	Run 1		Run 2		Run 3	
	Stage 1	Stage 2	Stage 1	Stage 2	Stage 1	Stage 2
Packing depth (m)	1.8	1.8	1.8	1.8	1.8	1.8
Superficial gas velocity (m/sec)	1.6	1.6	1.6	1.6	1.5	1.5
Charging current (milliamps)	14	36	13	33	15	42
Charging voltage (kilovolts)	32	30	33	31	33	31
Sparks/min	62	46	64	48	59	54

The Upjohn facility has a low energy wet scrubber that is intended primarily for chloride control. However, the scrubber provides some reduction of particulate emissions in the greater than 5 µm size range. The Upjohn scrubber is a single-pass, counter-current packed tower with an integral mesh-type demister. The key parameters that affect particulate control efficiency for this system are the scrubber liquid/gas ratio, the superficial gas velocity through the scrubber, and the pressure drop across the scrubber. The available data on the system are presented in Table 4-27.

Two of the facilities--Du Pont and TWI--used venturi scrubbers for particulate control. At Du Pont the gas streams from the two incinerator components entered separate quench chambers and venturi scrubber sections. Each stream has a nonreversing cyclone demister for droplet separation. Additional droplet separation is achieved in the absorption train and demister. At TWI the exhaust gases entered a small cyclonic spray quench chamber, followed by the venturi throat. A two stage chevron/mesh type mist eliminator with backup water sprays was used for droplet separation. The key parameters in both systems are the liquid/gas ratio in the venturi, the superficial gas velocity in the venturi throat, and the pressure drop across the system. These data are compiled with the data from Upjohn in Table 4-27. One other important parameter that was not directly measured is the droplet carryover from the mist eliminators. As indicated earlier, droplet carryover can contribute to the measured amount of particulates.

4.2.2.2 Performance of Particulate Emissions Control Systems--

Evaluation of the performance of the various particulate control devices is difficult, since inlet particulate data were obtained at only one site. Further, estimates of inlet concentrations at the other sites cannot reasonably be developed based on waste feed ash content. As a result, the discussion below addresses performance of the systems based primarily on their ability to achieve the emissions standard of 180 mg/Nm^3. The first paragraph below characterizes particulate emissions from the sites with no particulate control. The remaining paragraphs discuss the particulate emissions data for each of the sites with some type of particulate control.

Emissions data from the tests at Zapata, American Cyanamid, and Mitchell and the data from the inlet tests at Plant B are presented in Table 4-28. As indicated in the table, these results represent only facilities firing liquid wastes. The results show a wide range in the fraction of the ash that is emitted as particulate and varied abilities of plants with no particulate control equipment to meet the current particulate regulation. The data on fraction of the ash emitted as particulate indicate that Plant B and Mitchell emit approximately half of the ash as particulate while American Cyanamid emits nearly all of the ash as particulate. The results from Zapata were disregarded because: (a) wooden pallets are used to initiate combustion and probably contribute to particulate emissions; and (b) the waste samples for Runs 2 to 4 were not considered to be representative. In comparing the emission rates to the current standard, Zapata easily met the standard on all 3 tests and American Cyanamid met the standard on all but one test, but Mitchell exceeded the standard by a large margin on all three tests. The results from Mitchell and the last test at American Cyanamid

TABLE 4-27. SUMMARY OF PARTICULATE SCRUBBER DATA

Plant	Run	Liquid/gas ratio (L/Nm^3)	Superficial gas velocity (m/s)	Pressure drop (kPa)
Upjohn	2	11.5	0.31	[a]
	3	11.5	0.31	
	4	11.2	0.31	
Du Pont	1	[b]	[c]	32
	2			32
	3			32
TWI	1	1.9	[c]	4.0 (2.1)[d]
	2	-		3.8 (1.9)
	3	1.3		3.8 (1.8)
	4	1.2		3.8 (2.0)

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[a] No pressure data were recorded at Upjohn.

[b] Water flows to the scrubber were not available at Du Pont.

[c] Data are not sufficient to calculate venturi throat area at Du Pont and TWI.

[d] The first value includes pressure drop across venturi and mist eliminator. Value in parentheses is pressure drop across venturi.

TABLE 4-28. SUMMARY OF UNCONTROLLED PARTICULATE EMISSIONS DATA

Site	Run No.	Waste type	Ash input		Particulate emissions		Output/input (%)
			Concentration (%)	Rate (g/min)	Concentration (mg/Nm³)[a]	Rate (g/min)	
Plant B	2	Aqueous/organic liquid	4.82/1.07[b]	1,040	2,516[a]	490	47
	3		4.66/1.05	887	2,263[a]	431	49
Zapata	1	Liquid organic	0.018	0.12	69.1	0.83	690
	2		0.013	0.099	50.2	0.67	680
	3		0.0098	0.076	81.9	1.33	1,750
	4		0.14	1.1	38.5	0.67	61
American Cyanamid	1	Liquid organic	0.16	3.9	92.6	3.7	95
	2		0.19	3.2	171.1	4.5	140
	3		0.19	4.2	157	4.0	95
	4		< 0.05	< 0.16	15.0	0.43	270
	5		0.50	11.3	400	10.7	95
Mitchell	1	Aqueous/organic liquid	0.70	100	1,125	61	61
	2		0.78	127	719	39	31
	4		0.80	78	865	54	69

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[a] Concentration shown for Plant B is at the inlet to the control device (not the stack).

[b] First value is organic waste ash content and second value is aqueous waste ash content.

suggest that any facility firing liquid wastes with ash contents above about 0.5% will need some type of particulate control device to meet the standard.

Available particulate emissions data for the five facilities that have control equipment are presented in Table 4-29. Outlet data for Ross, Upjohn, Du Pont, and TWI are included as are both inlet and outlet data for Plant B. The paragraphs below discuss the data for each of the systems individually.

The most complete data are those collected at Plant B. These data indicate that a consistent fraction (about 50%) of the ash is entrained as fly ash and enters the control device. The device appears to be about 85% efficient. At this efficiency the Plant B system does not meet the emissions standard. In fact it exceeds the standard by a factor of more than 2, indicating that a control efficiency of about 95% would be needed to achieve the standard.

The Ross incinerator met the standard on all three runs. The comparison of ash input to particulate output had a very consistent ratio of 1.5%. Since the drum solid waste accounts for about 80% of the ash input and no data are available on the quantities of such ash emitted as particulate, no estimate of the efficiency of the ionizing wet scrubber could be developed.

The Upjohn facility failed to meet the particulate standard on both tests. The fact that the scrubber achieved little control was expected in that the packed bed scrubber provides little control for particles less than 5 µm in diameter. Available data suggests that most particles from hazardous waste incinerators are less than 2 µm in diameter.[8] However, the results are unusual in that the quantity of particulate emitted during the two tests are about three times the amount of ash in the waste feed. The facility would obviously have met the standard if the emissions had been reduced by a factor of three. No apparent reason for the discrepancy in the ash and particulate rates could be identified.

The Du Pont incinerator easily met the particulate standard on all three runs. This result was expected in that the venturi scrubber operated at a very high pressure drop (about 130 in H_2O). With pressure drops at this level, good control of even fine particles should be achieved.

The TWI facility met the particulate standard on three of the four runs and the four run average was 168 mg/Nm^3. No apparent difference in the waste feed composition or the venturi scrubber operating conditions were noted during Run No. 2 that would account for the higher particulate emission rate.

An overall average of the outlet particulate data is presented in Table 4-30. These data indicate that four of the eight sites tested failed to meet the particulate standard and that two others met the standard with less than a 20% margin. These data suggest that achievement of the particulate standard may be more difficult than achievement of either the DRE or HCl standard.

TABLE 4-29. SUMMARY OF PARTICULATE RESULTS FOR SITES WITH CONTROL EQUIPMENT

Site	Waste type	Control device	Run No.	Average stack Concentration (mg/Nm^3)[a]	Ash input rate (g/min)	Particulate output rate (g/min)	Output/ input (%)
Plant B (inlet)	Aqueous/organic liquid		2	2,516	1,040	490	47
			3	2,263	887	431	49
Plant B (outlet)	Aqueous/organic liquid		2	429	1,040	77	7.4
			3	371	887	64	7.2
Ross	Drum solids/ aqueous/ organic liquid	Ionizing wet scrubber	1	139	5,160	77	1.5
			2	176	6,390	92	1.5
			3	139	5,450	76	1.4
Upjohn	Liquid organics/gas	Packed bed scrubber	2	217	3.8	12	320
			3	183	3.5	9.7	280
DuPont	Liquid/solid	Venturi	1	33.7	229	9.8	4.1
			2	10.4	304	2.8	0.92
			3	24.8	431	7.0	1.6
TWI	Liquid/solid/ aqueous	Venturi	1[c]	172	3,590	9.3	0.26
			2[c]	290	4,120	21	0.51
			3[c]	110	3,740	8.8	0.24
			4[d]	102	1,220	6.7	0.55

[a] Corrected to 7% O_2.

[b] Value may be low due to sample filter leakage.

[c] Solid waste low BTU chlordane containing sand (~ 90% ash).

[d] Solid waste high BTU organics (~ 20% ash).

TABLE 4-30. SUMMARY OF PARTICULATE EMISSIONS RESULTS

Facility	Particulate control device	Average[a] outlet concentration (mg/Nm^3)
Ross	Packed tower Ionizing wet scrubber	151
Plant B (outlet) gas)		400
Zapata	None	60
Upjohn	Packed tower	200
American Cyanamid	None	208
Mitchell	None	900
Du Pont	Venturi scrubber	23
TWI	Venturi scrubber	168

[a] Corrected to 7% O_2.

4.2.3 Metals in Hazardous Waste Incinerator Effluent Streams

Metals contained in the waste feed to incinerators eventually exit from the incinerator by one of three pathways--as part of the particulate emissions (or vapor) from the stack, in liquid or solid effluents from the control device, or in the incinerator ash. Metals were analyzed in selected samples of these effluent streams from five of the eight facilities tested during this program. The analysis focused on the 12 metals identified in Appendix VIII as hazardous constituents--antimony, arsenic, barium, beryllium, cadmium, chromium, lead, mercury, nickel, selenium, silver, and thallium.

The results from those analyses provide some information on the distribution of the metals among the various effluent streams. However, the data on composition and flow rates are not sufficient to completely characterize the distribution of metals for any specific plant or for "typical" facilities.

The results are presented in three sections. The first section discusses air emissions of metals and the impact of control equipment on these emissions. The second section discusses the available data on ash and control device effluents. The final section presents an overall incinerator metals material balance.

4.2.3.1 Metals Content of Particulate Emissions--

Particulate samples were analyzed for metals content at five plants--Ross, Plant B (one run only), American Cyanamid (one run only), Du Pont, and TWI. A summary of the results of the particulate analyses in terms of both fraction of the particulate comprising hazardous metals and mass emissions rate of hazardous metals is presented in Table 4-31. Additional data are contained in Appendices C, D, G, I, and J.

As indicated in Table 4-31, most of the metals emissions were below detection limits for at least half of the runs. The notable exceptions were barium, cadmium, chromium, lead, and nickel which were quantifiable on at least one run at each of the five sites. The only metals that were emitted at rates greater than 1 g/min were antimony (one run at Ross), and lead (three runs at Ross and one run at TWI). Uncontrolled emission rates of selenium and lead at Plant B were also greater than 1 g/min.

Another factor of interest in Table 4-31 is the relative contribution of the hazardous metals to the total particulate loading at each of the five facilities. At Plant B these metals contributed about 1.5% of the total particulate at both the inlet and outlet. At both Ross and Plant B, the metals consistently contributed approximately 10% of the total particulate. The only plant which had significant variation in the hazardous metals content between runs was Du Pont which ranged from 3.3 to 10.4%. No reason for this wide variation could be identified. However, it appeared to be associated with the widely varied total particulate loadings.

Table 4-32 shows the percentage of each metal in the waste feed that was emitted as particulate. The most significant result from this view of the data is that Du Pont and Ross, which have high efficiency particulate controls, generally emitted a smaller fraction of metals than American Cyanamid or Plant B inlet (uncontrolled) or TWI and Plant B outlet which had less efficient controls. These data do suggest that metals emissions can be significantly reduced by high efficiency particulate controls.

The data also indicate that a high fraction of lead and a low fraction of barium were emitted, with other compounds showing a wide variation in fraction emitted with no discernible trend. These variations may be associated with either the volatility of the metal bearing compounds or the solubility of those compounds in the scrubbing liquid. Since the emission rates of specific compounds at inlets or effluents were not quantified, analyses of these mechanisms were not possible.

4.2.3.2 Metals in Ash and Control Device Effluents--

Evaluation of the quantity of metals in ash and control device effluents was limited by the paucity of data on both metals concentrations and mass flow rates for these streams. The only ash and effluent streams for

TABLE 4-11. SUMMARY OF PARTICULATE METALS EMISSIONS

Metal	Unit of measure	Ross			Plant B		American Cyanamid	Du Pont			TWI			
		Run 1	Run 2	Run 3	Run 2 inlet	Run 2 outlet	Run 3	Run 1	Run 2	Run 3	Run 1	Run 2	Run 3	Run 4
Antimony	µg/g particulate g/min	820 0.063	9,130 0.84	15,200 1.2	300 0.17	< 2,500 < 0.19	< 12,000 < 0.48	< 1,200 < 0.012	< 4,100 < 0.012	< 1,700 < 0.012	< 6,200 < 0.06	< 2,800 < 0.06	< 6,700 < 0.06	< 8,800 < 0.06
Arsenic	µg/g particulate g/min	< 300 < 0.023	< 240 < 0.022	< 300 < 0.024	< 72 < 0.035	< 650 < 0.050	- -	< 5,000 < 0.049	< 17,000 < 0.049	< 7,000 < 0.049	< 2,000 < 0.02	900 0.019	< 2,200 < 0.02	< 2,800 < 0.02
Barium	µg/g particulate g/min	1,250 0.096	590 0.054	690 0.052	250 0.12	930 0.072	< 1,000 < 0.04	648 0.0064	3,090 0.089	742 0.0051	770 0.0072	41 0.0087	480 0.0051	480 0.0032
Beryllium	µg/g particulate g/min	< 0.40 < 0.00003	< 0.32 < 0.00003	< 0.41 < 0.00003	5 0.002	< 43 < 0.003	- -	< 120 < 0.0012	< 420 < 0.0012	< 180 < 0.0012	< 12 < 0.0001	6.2 0.00013	< 12 < 0.0001	< 16 < 0.0001
Cadmium	µg/g particulate g/min	1,130 0.087	610 0.058	900 0.069	140 0.069	150 0.012	< 1,200 < 0.005	1,260 0.012	1,160 0.0033	953 0.0066	4,000 0.036	3,800 0.080	4,300 0.036	3,700 0.025
Chromium	µg/g particulate g/min	2,620 0.20	1,610 0.15	2,770 0.21	950 0.47	1,500 0.12	47,500 0.19	668 0.0066	- -	- -	1,500 0.014	830 0.017	1,000 0.087	1,000 0.0068
Lead	µg/g particulate g/min	91,600 7.1	68,900 6.4	96,100 7.3	3,100 1.5	5,300 0.41	< 4,000 < 0.016	10,700 0.11	31,100 0.089	35,100 0.24	95,000 0.88	96,000 2.0	100,000 0.87	100,000 0.68
Mercury	µg/g particulate g/min	56 0.0043	< 44 < 0.041	< 56 < 0.043	< 75 < 0.037	< 680 < 0.052	< 16,000 < 0.064	< 1,000 < 0.01	< 3,500 < 0.01	< 1,500 < 0.01	< 2,200 < 0.02	< 960 < 0.02	< 2,300 < 0.02	< 3,100 < 0.02
Nickel	µg/g particulate g/min	590 0.045	200 0.018	420 0.032	650 0.32	740 0.57	49,000 0.20	5,170 0.051	4,920 0.014	4,260 0.030	< 460 < 0.004	230 < 0.004	< 500 < 0.004	< 660 < 0.004
Selenium	µg/g particulate g/min	< 600 < 0.046	< 500 < 0.046	< 600 < 0.047	9,200 4.5	3,700 0.29	- -	13,800 0.14	61,600 0.18	28,300 0.20	< 49,000 < 0.5	< 22,000 < 0.5	< 53,000 < 0.5	< 70,000 < 0.5
Silver	µg/g particulate g/min	14.8 0.001	11.7 0.001	7.6 0.006	< 22 < 0.011	< 200 < 0.015	620 0.0025	648 0.0064	1,880 0.0054	222 0.0015	< 540 < 0.005	< 240 < 0.005	< 580 < 0.005	< 770 < 0.005
Thallium	µg/g particulate g/min	150 0.012	120 0.011	150 0.011	< 120 < 0.059	< 1,100 < 0.085	< 10,000 < 0.004	< 900 < 0.0089	< 3,100 < 0.0089	< 1,300 < 0.0089	< 4,000 < 0.04	< 1,800 < 0.04	< 4,300 < 0.04	< 5,700 < 0.04
Total hazardous metals	% of total particulate	9.8-9.9	8.1-8.2	11.6-11.7	1.5	1.2-1.7	9.7-14.1	3.3-4.1	10.4-13.2	7.0-8.3	10.1-16.6	10.2-13.9	10.6-17.5	10.4-19.7

Note: < indicates that the concentration of metal was below the detection limit.

TABLE 4-32. METALS EMISSIONS AS A PERCENTAGE OF METALS INPUT

Site	Air pollution control device	Run No.	Metals emissions/metals input (%)											
			Sb	As	Ba	Be	Cd	Cr	Pb	Hg	Ni	Se	Ag	Tl
Ross	Yes	1	a	a	0.16	b	0.96	0.88	8.4	a	0.42	a, b	a	a
		2	5.3	a	0.13	b	1.1	0.73	9.7	a, b	0.05	a, b	a	a
		3	9.1	a	0.13	b	12.3	1.2	11.4	a, b	0.26	a, b	a	a
Plant B - Inlet	No	2	14-19[c]	a, b	6.3	a, b	a	56	63-71[c]	a	200	56-82[c]	a	b
Outlet	Yes	2	a	a, b	3.8	a, b	a	14	17-20[c]	a	36	3.6-5.6[c]	a	b
American Cyanamid	No	3	a, b	b	a, b	a, b	a, b	34	b	b	47	b	a	b
Du Pont	Yes	1	b	a	1.6	a, b	3.1	0.43	4.2	a	0.28	a, b	a	a, b
		2	b	a	13.3	a, b	0.94	b	1.2	a	0.091	a, b	a	a, b
		3	b	b	0.75	a, b	2.4	b	1.8	a	0.25	a, b	a	a, b
TWI[d]	Yes	1	a, b	a, b	0.24	b	26	1.8	25	a, b	b	a, b	a, b	a, b
		2	a, b	a	0.26	b	50	1.9	51	a, b	b	a, b	a, b	a, b
		3	a, b	a, b	0.15	b	25	1.0	26	a, b	b	a, b	a, b	a, b
		4	a, b	a, b	0.24	b	37	1.8	43	a, b	b	a, b	a, b	a, b

[a] Amounts in waste inputs contained < values.

[b] Amounts in particulate samples contained < values.

[c] Portions of waste inputs contained < values.

[d] Based only on liquid organic waste and solid waste feeds.

which metals concentrations are available are: (a) the liquid effluent from the first absorber at Ross (upstream from the particulate control device); (b) the control device catch at Plant B; (c) the kiln ash sluice water from Du Pont; and (d) the chamber ash and water tank solids from TWI. The paragraphs below discuss the data from each of these sites for barium, cadmium, chromium, lead, and nickel. Because of the limited data no general conclusions are drawn.

The concentrations for the five metals in the absorber system effluent at Ross are shown in Table 4-33. As indicated in the table, the concentrations of both lead and cadmium exceed the EP toxicity limits. All other compounds were below that standard by a wide margin. The data in Table 4-33 may be biased high in that the scrubber system is primarily a recycle system with the effluent going to a pond and eventually recycled to the scrubber.

TABLE 4-33. CONCENTRATION OF METALS IN ROSS SCRUBBER EFFLUENT

	Concentration mg/L			EP toxicity limit
	Run 1	Run 2	Run 3	
Barium	2.58	1.92	1.47	100
Cadmium	1.28	1.27	1.17	1.0
Chromium	0.802	0.739	0.736	5.0
Nickel	0.293	0.238	0.438	-
Lead	14.1	13.3	12.0	5.0

The concentrations of each of the five metals in the Plant B control device ash and the concentrations of the metals in the leachate for EP toxicity are shown in Table 4-34. Although some of the metals are present at relatively high concentrations in the original sample, only cadmium exceeded the allowable EP toxicity limit.

The concentrations of metals in the Du Pont kiln ash sluice water and TWI chamber ash and tank solids are shown in Tables 4-35 and 4-36, respectively. Sufficient data were not available on total ash flow rates to calculate metals mass flow rates. As indicated in Tables 4-35 and 4-36 all ash samples at Du Pont and TWI were well below the EP toxicity limits.

4.2.3.3 Metals Balance--

A detailed metal balance was not performed at any single facility due either to sampling difficulties, difficulties in determining flow rates of bottom ash, or a preliminary indication that metals were not expected in the waste feeds at a given facility. However, a generalized material balance was derived based on the data collected at the five facilities for barium, cadmium, chromium, and lead. These four Appendix VIII metals were detected in most of the collected samples.

TABLE 4-34. CONCENTRATION OF METALS IN PLANT B CONTROL DEVICE ASH

Metal	Concentration in ash (mg/g)	Concentration in leachate (mg/L)	EP toxicity limit (mg/L)
Barium	1.6	0.17	100
Cadmium	0.13	2.0	1.0
Chromium	0.48	0.2	5.0
Lead	3.1	< 0.04	5.0
Nickel	0.09	0.2	-

TABLE 4-35. METALS CONCENTRATION IN DU PONT KILN ASH SLUICE WATER

Metal	Concentration (mg/L)			EP toxicity limit
	Run 1	Run 2	Run 3	
Barium	4.24	0.671	0.779	100
Cadmium	< 0.035	0.124	0.038	1.0
Chromium	0.499	0.665	0.952	5.0
Lead	0.477	2.03	0.494	5.0
Nickel	15.9	5.47	7.19	-

TABLE 4-36. METALS CONCENTRATION IN TWI CHAMBER ASH AND WATER TANK SOLIDS

Metal	Concentration									
	Run 1		Run 2		Run 3		Run 4		EP toxicity limit	Water tank solids
	Ash/leachate		Ash/leachate		Ash/leachate		Ash/leachate			
	mg/g	mg/L	mg/g	mg/L	mg/g	mg/L	mg/g	mg/L	mg/L	mg/g
Barium	0.19	0.36	0.28	0.34	0.21	0.46	0.31	0.80	100	4.2
Cadmium	0.0021	0.016	0.0022	0.023	< 0.002	0.0088	< 0.0021	0.0084	1.0	0.21
Chromium	0.07	0.014	0.091	0.013	0.066	< 0.007	0.18	0.015	5.0	0.73
Lead	0.081	0.12	0.11	0.10	0.094	0.058	0.079	< 0.04	5.0	8.0
Nickel	0.012		0.02		0.011		0.024			< 0.035

Table 4-32 lists the percentage of input metals appearing in stack effluent. The Plant B inlet gas and American Cyanamid data reflect an uncontrolled effluent and thus indicate a high proportion of input metal released. The Ross and Du Pont results represent metal release from facilities with adequate particulate control (i.e., meeting the current particulate standard). The Plant B outlet gas data are higher than the Ross and Du Pont data due most likely to the failure of the emissions control system at Plant B in meeting the particulate standard. The TWI data cannot be easily compared to the other data on the table. At TWI a significant amount of sand and gravel was in the feed material which affected the balance of ash and metals in the incinerator and control system.

Based on these results the following generalized material balance was derived:

	% of Input Metals	
	Average	Range
Incinerator with Particulate Control		
Metals emitted as particulate	3	0-27
Metals removed by scrubber	40	Not available
Metals in bottom ash	57	Not available
Uncontrolled Incinerator		
Metals emitted as particulate	43	0-60
Metals in bottom ash	57	Not available

Metals removed by a scrubber were calculated by subtracting controlled emissions from uncontrolled emissions. Material balance data were not available for bottom ash, thus the proportion of metals in the bottom ash was calculated as the portion of metals not emitted in the stack or removed by the scrubber.

4.3 QUALITY OF RESULTS

Data gathered during this study were used to assess how well hazardous waste incinerators perform and to evaluate various relationships between emissions data and process parameters. The quality of conclusions from these assessments is dependent on the quality of data generated during the eight incinerator tests.

Three of the more important questions that address the quality of the results of a trial burn or trial burn type test are:

- Are the results based on accurate and precise sampling and analysis data?
- Did monitoring of process conditions during the trial burn accurately reflect incinerator operating conditions?

- What procedures should be used to reduce data so that the final results most accurately reflect incinerator performance?

These three questions are addressed in the following subsections. The first subsection summarizes the QA/QC data from this program and discusses the implications of these data to the overall quality of results. The second subsection reviews the quality of process monitoring data. The final subsection describes data handling and reduction procedures that were used and discusses problems associated with data handling and reduction that were addressed during the program.

The subsections that follow do not provide complete answers to those three questions outlined above. Because this study was not intended as a methods development or methods validation study, the results from these tests are not adequate to fully quantify the precision and accuracy of the sampling and analysis methods used. Such a characterization can only come from complete methods validation studies. The results presented in the following subsections do provide an assessment of data quality, identify some of the factors which affect data quality and highlight the need for, and provide input to, future detailed validation studies.

4.3.1 Quality Assurance/Quality Control Results

4.3.1.1 Introduction--

The overall objective of the quality assurance activities associated with this program was to provide data of verifiable quality by making certain that: proper sampling and analysis methods were used; field sampling and laboratory equipment were adequately calibrated; standard field sampling and analysis protocols were followed; appropriate sample handling and transport procedures were followed; and chemical analyses were performed under controlled conditions. To realize this objective, QA/QC protocols were integrated into those tasks which impacted upon the sampling and analysis results. The QA/QC program for this study incorporated two primary aspects: (1) external quality assurance; and (2) internal quality assurance.

External quality assurance consisted of both system and performance audits of field and laboratory functions; the audits were conducted by an independent Quality Assurance Office. As part of the internal quality assurance program, standard operating procedures to assess and maintain quality of results were developed and followed by sampling and analysis personnel.

To assess precision, replicate analyses of samples were conducted and the percent relative standard deviation (%RSD) was calculated from the results. The percent relative standard deviation is defined as the standard deviation of the replicate measurements divided by the arithmetic mean value of the measurements times 100. To assess accuracy, the percent recovery (%R) was calculated for fortified and spiked samples. The percent recovery for spiked samples is defined as the amount found during analysis divided by the amount spiked times 100. For fortified samples the percent recovery is defined as the amount found in the fortified sample less the native amount found in the sample, divided by the amount fortified times

100. For external audits the accuracy assessment was essentially the same, although the definition is slightly different. For external audits the percent relative error was calculated; percent relative error (%RE) is defined as the amount found in the sample minus the actual amount in the audit sample, divided by the actual amount in the sample times 100. Note that the percent relative error plus 100 is equivalent to percent recovery (%RE + 100 = %R).

Conclusions derived from the QA/QC program and the pertinent results are summarized in the following sections. Section 4.3.1.2 provides an overall summary of the QA/QC program results and conclusions from these results. Section 4.3.1.3 provides a more detailed discussion of QA/QC results for volatile organic compounds, semivolatile organic compounds, and metals. Appendices K and L provide complete reports of results for the external quality assurance and laboratory internal quality assurance programs, respectively.

4.3.1.2 Summary and Conclusions--

Due to the broad scope of this program general conclusions from the QA/QC data are difficult to reach; almost any general conclusion will have some exception for one of the many compounds or samples analyzed from the eight different facilities. On the other hand, examining the QA/QC results for each compound for all tests and preparing a concise summary is nearly an insurmountable task. Consequently, the approach taken is to review and summarize the entire body of QA data as a means of identifying general trends and of assessing overall data quality. Specific cases where the QA/QC results indicate that general trends are not followed and that the results warrant special attention also are evaluated and discussed. In reviewing the QA/QC data, it is important to remember that data were obtained for a large range of different analytes and that general conclusions drawn from the reported data are not restricted to specific POHCs or PICs of interest for individual incinerator tests. Also, note that in tabulating and presenting the QA data reported in Appendix L and summarized in this section, no attempt was made to remove outliers or poor results likely explainable by specific problems such as analyte concentrations near the detection level or outside the linear range of the analytical instrument.

In most cases sufficient quality assurance data were obtained to verify the overall quality of the test data. The results of both the external and internal quality assurance programs indicate that established quality assurance protocols were followed and that the overall quality of the field and laboratory work was generally adequate to meet the objectives of this study. The external audit program results indicate that the overall performance and conduct of the field and laboratory work can be judged to be adequate and acceptable; more specifically:

- The field systems audit determined that the protocols and procedures were followed.

- The field performance audits determined that the equipment was calibrated and that it performed properly.

- Laboratory systems audits determined that laboratory procedures were performed in an acceptable manner.
- Laboratory performance audits indicated the volatile and semivolatile organic compound analysis was accurate and precise; the trace metals analysis was accurate and precise with the exception of selenium analysis for the TWI samples; the chloride analysis was accurate and precise.

Results of the laboratory internal quality assurance program indicate that, overall:

- Analyses of volatile and semivolatile organic compounds were precise, generally within RSD $\leq$ 30% for replicate analyses.
- The level of accuracy (percent recovery) obtained during organic compound analysis was generally within expected ranges considering the complex sample matrices involved; the majority of the data were within the expected recovery range of 50 to 130%. This accuracy directly impacts the measured amounts of a compound in and out of an incinerator.
- Better accuracy (percent recovery) was obtained for volatile compounds than for semivolatile compounds.
- The fact that better percent recoveries for organic compounds were obtained for external audits than for actual samples is a strong indication that complex sample matrices do affect analytical results.
- Metals analyses were accurate and precise.

Because of the analytical procedures ("internal calibration") followed for analysis of the VOST samples, no volatile compound recovery data, were obtained for VOST samples during the QA program. The reason for this is that the analytical procedure involves obtaining actual response factors for the individual analytes by spiking a blank Tenax/charcoal trap with known quantities of an internal calibration standard and of the analytes of interest. The same internal standard is then spiked onto the actual sample traps just prior to analysis, and the sample is quantified based on the response factor established from the spiked blank.

Although no recovery data could be obtained for VOST, a laboratory evaluation of VOST was conducted prior to this field sampling program to assess the accuracy and precision of the sampling method. Results of this laboratory evaluation indicate that the method can measure at the level and accuracy needed to demonstrate achievement of a 99.999% DRE, well above the current regulatory limit of 99.99% DRE. Results of this evaluation are discussed in more detail later in this section.

As expected for a program of this size, the analytical accuracy and/or precision obtained was less than desired for some specific cases. These were often isolated cases, e.g., poor precision for a specific test site. However, the quality assurance program results did identify some apparent systematic biases; e.g., consistently poor recoveries from all samples for a specific compound. Specific problems encountered which are discussed in more detail later in this section include:

- Low volatile organic compound recoveries from aqueous waste samples.
- Low recovery for the volatile compound cis-1,4-dichloro-2-butene.
- High recoveries for volatile organic compounds from the Upjohn waste samples.
- Erratic recovery and poor precision for phenol (a semivolatile).
- Erratic recovery and poor precision for naphthalene (a semivolatile).
- Low recovery for aniline (a semivolatile) from XAD.
- Low recovery for bis(2-ethylhexyl)phthalate (a semivolatile).

The conclusions summarized above are discussed in the paragraphs which follow. Specific areas which are discussed in more detail include: comparison of external and internal QA program results; results of the laboratory evaluation for the VOST; accuracy results for semivolatile organics; and, results for the surrogate compounds used during the QA program.

Table 4-37 compares the relative accuracy results obtained for the external audits and internal quality assurance checks for volatile and semivolatile organic compounds. In general, better accuracy was obtained for the external audits than for the internal checks; this is an indication that the complex matrices of the samples do affect the analytical results.

TABLE 4-37. COMPARISON OF EXTERNAL AND INTERNAL QUALITY ASSURANCE RELATIVE ERROR RESULTS

	External audits		Internal audits	
	No. of samples	Percent of samples with relative error ≦ 30%	No. of samples	Percent of samples with relative error ≦ 30%
Volatile organic compounds	751	97	130	51
Semivolatile organic compounds	391	93	903	45

Tables 4-38 and 4-39 compare the internal and external relative accuracy results by compound for volatile and semivolatile organic compounds, respectively.

Prior to initiating the field sampling program, a laboratory evaluation of the VOST was conducted. The purpose of this evaluation was to assess the accuracy and precision of the sampling method for measuring volatile organics. The laboratory evaluation consisted of measuring percent recoveries for four different compounds at four different concentrations spiked into a synthetic stack gas. Percent recoveries were determined for vinyl chloride, trichloroethylene, carbon tetrachloride and chlorobenzene, each at concentration levels of 0.1, 1.0, 10.0 and 100 ng/L. Results of this laboratory evaluation indicate that for the two lowest concentration levels the percent recovery for a single test ranged from 38% to 173%. For the two highest concentrations, results of any single test ranged from 70 to 142% recovery, except for vinyl chloride which experienced sample train breakthrough for the highest concentration level. These results indicate that the method permits differentiating between a DRE of 99.99% and 99.999% since the order of magnitude difference in these DREs is greater than the variability (38 to 173%) noted during the laboratory evaluation.

Table 4-40 summarizes the accuracy (percent recovery) results for the internal quality assurance program. The results of the quality assurance program indicate that better accuracy generally was obtained for analysis of volatile compounds than for analysis of semivolatiles. Percent recovery was within the 70 to 130% range for 60% of the volatile QA samples compared to 46% of the semivolatile QA samples. The preparation of samples for analysis of semivolatile organic compounds requires more steps, i.e., extraction of the sample with a solvent followed by evaporative concentration of the solvent extract. It is not surprising that lower recoveries were obtained for semivolatiles.

Although the recoveries for each volatile and semivolatile were often outside the desired range, a number of samples were close to the desired range. If the percent recovery range is increased to 50 to 130%, then 70% and 64% of the volatile and semivolatile QA samples are within the range, respectively.

QA/QC results for volatile compounds generally were good. However, low recoveries for spiked analytes in aqueous wastes did appear to be a trend for several analytes at several sites. This includes carbon tetrachloride at Mitchell and TWI, toluene and trichloroethylene at Mitchell, and chloroform at TWI. The fact that poor recoveries were obtained for these spiked analytes should not impact on the test results, since these compounds were found at very low native levels. Even if the native levels were higher than reported, calculated DREs would be greater and general conclusions would not be affected. The important factor to consider from these data is that the potential exists for poor recoveries of certain volatiles from aqueous wastes. Since good precision was obtained during the analyses of the various QA/QC samples, the low recoveries indicate that, in each case, a systematic bias occurred.

TABLE 4-38. COMPARISON OF EXTERNAL AND INTERNAL QUALITY ASSURANCE RELATIVE ERROR RESULTS FOR VOLATILE ORGANIC COMPOUNDS

	External audits		Internal audits	
	No. of samples	Percent of samples with relative error ≦ 30%	No. of samples	Percent of samples with relative error ≦ 30%
Chloroform	83	100	38	39
Carbon tetrachloride	83	95	37	57
Trichloroethene	83	99	-	-
Benzene	83	98	17	59
Tetrachloroethane	29	100	-	-
Toluene	83	98	17	41
Methylene chloride	68	94	6	83
1,1,1 Trichloroethane	38	100	-	-
3,4-Dichloro-1-butene	8	88	-	-
Tetrachloroethene	68	100	-	-
Chlorobenzene	33	97	6	100
Bromodichloromethane	24	100	-	-
cis-1,4 Dichloro-2-butene	4	100	3	0
Bromoform	25	80	-	-
Methylene bromide	13	100	6	33
Bromochloromethane	13	100	-	-
Dibromochloromethane	13	100	-	-
Total	751		130	

TABLE 4-39. COMPARISON OF EXTERNAL AND INTERNAL QUALITY ASSURANCE RELATIVE ERROR RESULTS FOR SEMIVOLATILE ORGANIC COMPOUNDS

	External audits		Internal audits	
	No. of samples	Percent of samples with relative error ≦ 30%	No. of samples	Percent of samples with relative error ≦ 30%
Phenol	19	84	48	8
*Decafluorobiphenyl	26	100	200	45
*D_8-Naphthalene	29	93	188	47
Naphthalene	39	97	58	53
Hexachlorobenzene	25	100	22	77
*D_{12}-Chrysene	26	88	159	48
Bis(2-ethylhexyl)phthalate	38	74	19	58
m-Dichlorobenzene	12	100	9	56
p-Dichlorobenzene	12	100	6	83
2,4-Dimethylphenol	11	73	16	44
1,2,4 Trichlorobenzene	10	100	37	62
Diethyl phthalate	4	100	16	82
Aniline	3	100	6	33
Nitrobenzene	3	100	6	83
o-Nitrophenol	3	100	-	-
2-Nitrotoluene	3	100	-	-
2-Aminophenol	2	50	5	0
Quinoline	3	100	-	-
4-Aminophenol	1	100	-	-
m-Dinitrobenzene	3	100	-	-
p-Nitrophenol	3	100	-	-
Isophorone	2	100	4	100
Dodecanol	2	100	6	67
Butylbenzyl phthalate	2	50	6	33
3-4-Dichloro-1-butene	7	100	6	0
Trans 1,4-dichloro-2-butene	9	100	6	0
o-Chlorotoluene	9	100	6	67
Benzyl chloride	9	100	9	22
Hexachloroethane	9	100	9	22
Methylbenzyl chloride	9	89	6	0
Tetrachlorobutene	9	100	9	22
p-Chlorophenol	9	78	5	0
Hexachlorobutadiene	8	100	6	50
Hexachloropentadiene	8	100	6	0
Octachlorocyclopentene	8	100	6	50
Dibutyl phthalate	8	100	6	67
Chlordane	8	100	6	17
Total	391		903	

* Surrogate compound.

TABLE 4-40. SUMMARY OF RESULTS FOR INTERNAL QA PROGRAM

	Volatile organic compounds	Semivolatile organic compounds
Precision:		
Number of Measurements[a]	158	261
Number of compounds	15	37
Percent of total measurements with the %RSD ≤ 30%	89	76
Accuracy:		
Number of measurements	421	947
Number of compounds	12	37
Percent of total measurements with 70% ≤ recovery ≤ 130%	60	46
Percent of total measurements with 50% ≤ recovery ≤ 130%	70	64

[a] A measurement is defined as a set of replicate analyses.

Reaction of the analytes within the sample is one explanation; spiking of the analyte at levels above the solubility of the analyte in the sample is another. It is believed that the latter occurred in at least some cases, e.g., the TWI samples.

Like other volatile organics spiked into aqueous waste samples, the recovery of methylene bromide spiked into the aqueous waste sample from TWI was significantly less than 100%; the average recovery was 60%. In this case, the inaccuracy in measuring waste feed concentration could affect the results since the calculated DRE for this compound was just under 99.99%. A higher waste feed concentration would increase the DRE.

For the Du Pont samples, 0% recoveries were obtained for the spiked compound cis-1,4-dichloro-2-butene even though high native amounts were present in the original sample. Based on the results for this single set of samples, calculated DRE's for this compound appear not to be reliable. This compound hydrolyzes in the presence of water, and this reaction is the suspected reason for the low recoveries in the spiked samples. Reactions within the sample matrix to decompose an analyte is a plausible explanation for the low percent recovery data obtained for this compound and for other compounds. This potential problem merits further study and perhaps modification of some of the sample handling and analysis protocols. For example, it may be desirable: (1) to cold store reactive waste samples; and (2) to reanalyze an unspiked waste sample the same day as the spiked sample in order to observe any changes which may have occurred.

Percent recoveries for volatiles from the Upjohn waste samples were extraordinarily high (in excess of 400% for carbon tetrachloride, trichloroethylene, toluene, and chloroform). No explanation is available for these results. The analytical results for external audit samples for this data set were accurate and do not indicate that any particular analytical problems should have been expected (e.g., instrument calibration). Due to the abnormally high recovery values for these QA samples, there is some question as to the quality of the Upjohn volatile results. If one assumes the reported volatile concentrations in the waste samples are actually lower than reported then the reported DREs would be biased high.

In general, recoveries obtained for spiked semivolatile samples were within the expected 50 to 150% range. However, several apparent systematic biases appear in the QA/QC data for semivolatile organics. The four compounds for which potential analytical problems exist include phenol, naphthalene, aniline, and bis(2-ethylhexyl)phthalate.

The internal QA data for phenol indicate recoveries which are biased high for aqueous waste, organic waste, and spiked XAD samples. Recoveries greater than 150% were obtained for 80% of the aqueous and organic waste samples fortified with phenol; similarly recoveries of greater than 150% were obtained for 45% of the XAD samples spiked with phenol. The range of recoveries from the XAD varied considerably from 36-350%; the relative standard deviation of percent recovery from all spiked XAD samples was high (65%) which indicates poor precision for this measurement. All recoveries from the spiked water fraction (stack sampling train) were low; 100% of the values were below 50% recovery. This low recovery is likely explained by the high solubility of phenol in water and the inability of methylene chloride to extract the phenol from the water. Phenol was a POHC at Ross, Plant B, and Mitchell. Based on the QA results, the phenol results from the sites are suspect. However, when considering whether or not DREs are greater than 99.99%, only the results from Plant B are questionable. Measurement bias for the other two sites appear not to change the status of the calculated DRE in relation to 99.99%

Naphthalene was a POHC at five different test sites--Ross, Plant B, Mitchell, Du Pont, and TWI. Like phenol, the QA results for naphthalene indicate recoveries from XAD that are biased high (mean recovery of 162% for 21 samples); 43% of the QA samples had a recovery exceeding 150%. Again, the overall measurement precision was poor with a relative standard deviation of 74% for all relative accuracy samples (measurement precision for triplicate analyses within each set of QA samples was considerably better). In general, recovery results for the organic waste and spiked water fraction were better than for phenol. Eighty-three percent of the water fraction samples had recoveries in the 50 to 100% range; the mean recovery was 77% with an overall standard deviation of 25%. The mean recovery for organic waste samples was 93%; however, measurement precision was poor with an overall relative standard deviation of 67%. Aqueous waste samples from only two sites were spiked; recoveries at Plant B were good, but at Ross were very poor (0%). Results of the quality assurance data for naphthalene and review of the test data from the various sites indicate that the naphthalene results are suspect. In regards to whether or not measurement bias affected calculated DREs in relation to 99.99% DRE, review of the test data indicate that the status of the Ross, Plant B, and DuPont sites might be questionable. The affect of the measurement error on the naphthalene DRE cannot be accurately calculated.

Aniline was a POHC at three facilities--Ross, American Cyanamid and Upjohn. Recoveries from the single set of XAD samples from American Cyanamid indicate very poor recoveries of aniline from XAD. The mean recovery was 7%. However, recoveries from the water fraction were good; a mean recovery of 75%. No internal quality assurance data were obtained for aniline from the waste samples due to the very high native concentrations in the waste. This one set of data suggests that additional recovery data should be obtained for aniline in order to validate the method.

The QA results for bis(2-ethylhexyl)phthalate, indicate poor recoveries from the organic waste samples at the two sites for which internal audits were conducted (TWI and Upjohn). The percent recoveries for all organic waste audits were less than 50%. If the actual feed values were higher than measured, the DRE's would have increased. The poor QA results for this compound indicate that a problem may exist for measuring bis(2-ethylhexyl)phthalate. This compound is also known as a common contaminant which may confuse some of the QA data.

In general, results for the surrogates used during the study were comparable to results obtained for the other compounds analyzed; these results indicate that the surrogates can be used to assess overall data quality. Nonetheless, results less than ideal were noted for the surrogates, and improved performance would be desirable. For some of the analyses, high recoveries were obtained for the volatile surrogate D_4-1,2-dichloroethane; these recoveries indicate that mass spectral interference from other compounds in the sample matrix was occurring and that a compound which elutes earlier might provide improved results. No unusual results were noted for the surrogate D_{10}-ethylbenzene. For the analysis of organic waste samples, results for the semivolatile surrogates D_8-naphthalene and decafluorobiphenyl were biased high part of the time; this indicates interference from compounds in the sample matrix. On the other hand, results for the surrogate D_{12}-chrysene were biased low (recoveries in the 0 to 50% range for 57% of the QA samples analyzed) indicating a propensity for loss of this surrogate from the sample. Use of additional surrogate compounds in future tests to obtain more data for evaluation is desirable.

4.3.1.3 Results--

4.3.1.3.1 External quality assurance program--Field audits were conducted during the Ross, Plant B, and Du Pont tests. These audits indicated that no serious problems were encountered and that the sampling devices audited were performing in an acceptable manner. Sample handling and the resulting sample traceability also were deemed acceptable.

Laboratory performance audits for volatile and semivolatile organic compounds, metals, and chlorides were conducted for each set of test samples. The results of these audits are separately discussed in the following paragraphs.

A total of 751 external audit measurements were conducted for 17 different volatile organic compounds. Of these audits, 92% of the samples were measured with a relative error of less than or equal to ±20%; 98% of the samples were measured with a relative error of less than or equal to ±30%. The average relative error for each of the 17 compounds ranged from -17 to +10%; only five of the compounds analyzed had any value which exceeded ±30% relative error. Only the analysis for bromoform exhibited generally poor results; 20% of the bromoform audit values exceeding ±30% relative error. Bromoform is known to exhibit poor purging efficiency.

A total of 391 external audits were conducted for 37 different semivolatile organic compounds. Of these audits, 85% of the samples were measured with a relative error of less than or equal to ±20%; 93% of the samples were measured with a relative error of less than or equal to ±30%. The average relative error for individual compounds ranged from -54% (-26% was next lowest value) to +15%. The two extreme negative relative errors were isolated cases; only two audit samples were analyzed for each of the two compounds (2-aminophenol and butyl phthalate). In each case, one of the two samples analyzed exhibited poor recovery. The majority of compounds analyzed had mean relative errors of less than ±5%. Only 11 of the 37 compounds analyzed had any audit value which exceeded ±30% relative error.

In addition to the poor relative errors obtained for 2-aminophenol and butyl phthalate, the analysis of two other compounds exhibited poor precision. Bis(2-ethylhexyl)phthalate exhibited poor precision (43% of the audit values exceeded a relative error of ±20%), although the mean relative accuracy was 15%. Analysis of 2-4,dimethylphenol also exhibited poor precision (73% of audit samples exceeded a relative accuracy of ±20%); the mean relative error was 11%.

The results of the accuracy measurements for the three semivolatile surrogates were good. Results of the external audits yielded mean relative errors of -2.4%, 1.5%, and 0.4% for decafluorobiphenyl, D_8-naphthalene, and D_{12}-chrysene, respectively. Precision of the analyses also were good with calculated relative percent precisions of 10.4, 17.4, and 19.6% for the three compounds, respectively.

A total of 21 chloride audit samples were analyzed. No problems were encountered and the mean relative error was 1.2%.

A total of 136 audit samples for 14 different metals were analyzed. Of the total analyses, the relative error was less than or equal to ±20% for 95% of the samples; the relative error was less than or equal to ±30%

for 96% of the samples. Only five of the 14 metals analyzed had any audit with a relative error value that exceeded ±30%. The only serious problem noted during the audits was for selenium; the accuracy and precision of the selenium audits conducted on one of 3 days were unacceptable; the average relative error for this one day was 190%.

4.3.1.3.2 Internal quality assurance program--Internal quality assurance checks were conducted for each set of samples collected from the different test sites. The checks conducted included surrogate spiking and POHC fortification to assess accuracy (percent recovery), and analysis of replicate samples to assess analytical precision (relative standard deviation). The results of these internal quality assurance checks are discussed in the following paragraphs. Due to the large number of samples analyzed, the results are presented in a generalized manner for the entire data set and are not presented individually for each test site. Appendix K presents the complete results obtained for quality assurance checks at individual test sites.

Table 4-41 summarizes the overall results of the internal quality assurance precision and accuracy checks for volatile compounds. During this program, triplicate analyses were conducted on a total of 158 samples to assess measurement precision for 15 different compounds. Eighty-nine percent of the measurements had a relative standard deviation (RSD) of less than or equal to 30%. Measurement precision for the two surrogates (D_4-1,2-dichloroethane and D_{10}-ethylbenzene) was about the same as for the other compounds; 90% of the surrogate measurements had a RSD less than or equal to 30%.

A total of 421 samples were spiked with analytes to assess the accuracy for 12 different volatile compounds. The percent recovery was within the 70 to 130% range for 60% of the total measurements (see Table 4-41). However, an additional 10% of the samples were close to the desired range. If the range is increased to 50 to 130% recovery, 70% of the total measurements fall within the range. In general, the results indicate that percent recoveries were slightly better for the two surrogate compounds than for the other compounds. The results indicate that the recoveries for the aqueous waste samples generally were poorer than for the organic and drum waste samples. Sixty-six percent of the organic waste measurements were within the 70 to 130% recovery range, compared to only 48% of the aqueous waste measurements. Of the high recovery values (> 130% recovery) obtained, 47% of the aqueous waste high values were due to the surrogate D_4-1,2-dichloroethane; 29% of the high recovery values obtained for the organic waste samples also were due to this surrogate. These high results for this surrogate suggest that the compound is subject to interferences by other compounds and that a different volatile surrogate might perform better.

Table 4-42 summarizes the overall results of the internal quality assurance precision and accuracy checks for semivolatile compounds. During this program, triplicate analyses were conducted on a total of 261 samples to assess measurement precision for 37 different semivolatile compounds.

TABLE 4-41. SUMMARY OF VOLATILE COMPOUNDS INTERNAL QUALITY ASSURANCE RESULTS

Precision (replicate analyses)

Sample type	No. of compounds	No. of measurements[a]	Percent of total measurements with ≦ 30% relative standard deviation
Aqueous waste	13	41	88
Organic waste	15	117	89
All samples:			
All compounds	15	158	89
Surrogates only	2	40	90
All compounds, excluding surrogates	13	118	89

Accuracy (percent recovery)

Sample type	No. of compounds	No. of measurements[a]	Percent of total measurements in stated recovery (R) range		
			70 ≦ R ≦ 130	50 ≦ R ≦ 130	R > 130
Aqueous waste	9	118	48	62	13
Organic waste	12	303	65	77	13
All samples:					
All compounds	12	421	60	70	14
Surrogates only	3	236	68	80	11
All compounds, excluding surrogates	9	185	50	67	16

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[a] Waste sample measurements.

TABLE 4-42. SUMMARY OF SEMIVOLATILE COMPOUNDS INTERNAL QUALITY ASSURANCE RESULTS

Precision (replicate analyses)

Sample type	No. of compounds	No. of measurements	Percent of total measurements with ≦ 30% relative standard deviation
Aqueous waste:	17	35	65
Organic waste:	37	84	79
Water fraction:	32	65	91
XAD:	37	77	66
All samples:			
All compounds	37	261	76
Surrogates only	3	72	86
All compounds, excluding surrogates	34	189	72

Accuracy (percent recovery)

Sample type	No. of compounds	No. of measurements	Percent of total measurements in stated recovery (R) range		
			70 ≦ R ≦ 130	50 ≦ R ≦ 130	R > 130
Aqueous waste	10	86	58	68	12
Organic waste	21	293	34	49	28
Water fraction	31	238	55	75	4
XAD	37	330	46	68	14
All samples:					
All compounds	37	947	46	64	16
Surrogates only	3	603	46	64	12
All compounds, excluding surrogates	34	344	46	60	20

Seventy-six percent of the measurements (replicate analyses) had an RSD ≦ 30%. Measurement precision for the three surrogate compounds (decafluorobiphenyl, D_8-naphthalene, and D_{12}-chrysene) was slightly better than the combined precision for the other compounds; 86% of the surrogate replicate measurements had an RSD ≦ 30%.

A total of 947 samples were spiked with analytes to assess the accuracy for 37 different semivolatile compounds. The percent recovery for these compounds was within the 70 to 130% range for 46% of the total measurements (see Table 4-42). If the range is increased to 50 to 130% recovery, 65% of the total measurements fall within the range. The results indicate that percent recoveries for the three surrogate compounds are the same as the combined percent recovery of the other compounds. The results indicate that the recoveries for the aqueous waste samples were generally better than the recoveries for the organic and drum waste samples. For the aqueous waste, 58% of the samples were within the 70 to 130% recovery range; 34% of the organic waste samples were within this range. For the organic waste samples, a total of 27% of the surrogate decafluorobiphenyl values and 39% of the surrogate D_8-naphthalene values exceeded 130% recovery. None of the surrogate D_{12}-chrysene values exceeded 130% recovery, but 57% of the D_{12}-chrysene values showed less than 50% recovery. It appears that in complex organic wastes, D_{12}-chrysene shows a propensity for loss from the sample, and the two other surrogates show some propensity for interference in complex waste samples.

For metals, a number of the precision measurements were conducted using only duplicate samples, which makes these data less meaningful. However, the results indicate that precision generally was better than 30% RSD (see Table 4-43). Because of the large number of analytes and the relatively less importance of the data with respect to the overall program, duplicate samples were spiked blindly and prepared and analyzed at the same time as the unknown samples. As a result, some of the metals were not spiked at the desired level of one to two times the native level, and in some cases meaningful recovery data were not obtained. However, when the metals were spiked at appropriate levels, the recoveries were generally good. Recovery data were obtained for a total of 228 samples for 23 different metals. The percent recovery was within the 70 to 130% range for 85% of these samples (see Table 4-43). Problems were encountered with silver chloride precipitation during sample preparation; consequently, no recovery results are reported for silver.

4.3.2 Process Monitoring Data

Accurate determination of key process data varied greatly from facility to facility. Three parameters which are basic to any combustion process--temperature, residence time, and excess air--posed particular difficulties in obtaining values representative of combustion conditions. An overall heat/mass balance was performed in an attempt to assess the reliability of these values. The subsections below discuss some of the difficulties in determining process parameters and an evaluation of the reliability of these values based on the results of the heat balance calculations.

TABLE 4-43. SUMMARY OF METALS PRECISION AND ACCURACY DATA FOR INTERNAL CHECKS

	Precision		Accuracy	
Metal	No. of samples	Percent of samples with RSD ≦ 30%	No. of samples	Percent of samples with relative error ≦ 30%
Al	6	83	-	-
Ag	-	-	-	-
As	-	-	14	71
B	8	63	11	64
Ba	7	86	12	67
Be	2	100	19	84
Ca	7	100	3	100
Cd	3	100	21	81
Co	4	100	7	100
Cr	6	100	10	90
Cu	8	75	6	33
Fe	8	88	2	100
Hg	1	100	18	72
K	5	100	-	-
Mg	7	86	3	100
Mn	7	100	9	89
Mo	4	100	5	100
Na	7	86	-	-
Ni	4	100	19	89
P	6	83	7	71
Pb	5	100	9	78
Sb	2	50	18	78
Se	-	-	11	55
Sn	3	100	7	71
Ti	6	50	7	86
Tl				
Y	1	0	7	100
Zn	6	83	3	67
Total	123		228	

4.3.2.1 Problems in Determining Process Parameters--

The rate of oxidation of POHCs and associated incinerator performance are dependent on the time/temperature profile to which the POHCs are exposed in the incinerator and the availability of oxygen for reaction in the combustion chamber. Actual reaction rates are dependent on microscale conditions within the incinerator. Incineration conditions are generally estimated by the residence time and combustion temperature in the chamber, and the oxygen content (or excess air) in the exhaust gases from the chamber. However, even the determination of these parameters was not straightforward, as described in the following paragraphs.

Combustion temperatures were measured using a thermocouple located at some point or points in the combustion process at each facility. Due to the difference in geometries and thermocouple locations, measurement of the combustion temperature showed little comparability from plant to plant. These inconsistencies may affect any conclusions from the data which involve temperature or temperature related values.

The residence time in the combustion chamber is obtained by dividing the chamber volume by the volumetric flow of combustion gases through the chamber. However, because combustion chamber flow rates are not measured directly, the residence times reported in the Appendices C through J for each facility were calculated using the stack flow rate as a substitute for combustion chamber flow rate. During the testing of the eight incinerators the possibility for air to enter the process after the combustion chamber but prior to the stack sampling location was sometimes noted. A significant amount of this "inleak" air entering the system results in a combustion chamber flow rate that is biased high and a residence time that is biased low.

The estimate of excess oxygen available for reaction in the combustion chamber was also based on O_2 concentrations monitored in the stack gas. As with the residence time calculations, significant quantities of inleak air will result in an estimate of excess O_2 that is biased low if stack gas O_2 concentrations are assumed to be representative of excess O_2 in the combustion chamber exhaust gases.

To evaluate the potential for inleak air and the corresponding potential error in estimates of residence time and O_2 concentrations at the combustion chamber exhaust, heat balance calculations were performed. These calculations provide alternate estimates of the gas flow rate through the incinerator and concentrations of O_2 and CO_2 at the combustion chamber exit that can be compared to the measured stack values.

4.3.2.2 Heat Balance Procedure--

A brief outline of the method used for the heat balance calculations is included in the following paragraphs.

1. The Total Heat Input is calculated from the higher heating value (HHV) for all waste and fuel streams entering the combustion chamber(s). The HHV is based on the amount of heat given off from the burning of a sample of waste in an oxygen bomb and returning the combustion products (CO_2 and H_2O) to Standard Temperature and Pressure. Thus, the H_2O formed

in the reaction is returned to the liquid state, and the latent heat of condensation is included in the measured HHV.

2. An ultimate analysis was performed on samples of waste from each of the plants. This analysis yields values for percent carbon, percent hydrogen, percent nitrogen, etc., and percent oxygen (by difference). The percentages of hydrogen and oxygen include any H_2O present in the sample. In making the heat balance calculation, all of the oxygen in the waste was assumed as present as H_2O, or as forming H_2O in the combustion reaction. The amount of hydrogen consumed in forming the H_2O could then be calculated. The remaining hydrogen was assumed to be combined with carbon, in order to construct a composite waste stream consisting only of carbon and hydrogen. In the calculations, this stream was reacted with stoichiometric air to form CO_2 and H_2O (liquid). This step determines the amount of stoichiometric combustion air necessary (N_2) and the flow rates of CO_2 and H_2O leaving the combustion chamber.

3. The amount of heat needed to vaporize all of the water and then heat all of the gases up to the measured combustion chamber temperature was calculated using the heat capacities of H_2O, N_2, and CO_2.

4. Five percent of the Total Heat Input was subtracted as an assumed heat loss from the incinerator. The heat from Step 3 was also subtracted from the Total Heat Input. The remaining heat is the Excess Heat available to heat up Excess Air in the combustion chamber.

5. The amount of Excess Air was determined by dividing the Excess Heat value by the amount of heat required to raise a given amount of air up to the combustion chamber temperature.

6. The exit gas from the combustion chamber consists of the Excess Air from Step 5 and the H_2O, CO_2 and N_2 from Step 2. Knowing the composition and flow rate of the exit gas, values can be calculated for residence time, percent O_2 in the chamber and percent CO_2 in the chamber.

7. The inleak of air after the combustion chamber was calculated as the difference between the gas flow rates calculated in Step 6, and the measured stack flow rate. This inleak was calculated as a percentage of the measured stack flow rate. As a check, the O_2 and CO_2 in the combustion chamber exit gas was combined with the calculated O_2 in the inleak air and compared with the percent O_2 and CO_2 values measured in the stack.

4.3.2.3 Results of Heat Balance--

The results based on use of the above procedures for each of the eight test sites are presented in this subsection. These results should be viewed with caution in that the heat balance calculation is sensitive to changes in waste feed composition, temperature, and enthalpy values. The waste feed analysis is assumed to be representative of the average composition of the stream throughout the run. This assumption is suspect for some situations. The temperature used for the calculation is an average temperature measured by a thermocouple during the run. Whether or not the thermocouple gives an accurate reflection of the temperature within the chamber depends on location, type and accuracy of the measuring device. As indicated in Section 4.3.2.1 the incinerators varied significantly with respect to thermocouple location. For this calculation, a 50°F variation in temperature would result in a 5 to 10% variation in the calculated values. Literature values for heat capacities of gases vary, and a check of three or four sources indicate that the values used here may have been at the higher end of the range. A lower set of heat capacities would yield inleak values from 5 to 10% lower.

The heat balance calculation yields two sets of numbers. A set of conditions for the combustion chamber (percent O_2 and CO_2, flow rate, residence time and excess air) are presented in Table 4-44. These can be compared with the measured values for stack flow rate and the residence times calculated from the stack measurement also found in Table 4-44. The second set of numbers from the heat balance are the concentrations of O_2 and CO_2 in the stack which are compared with Orsat and continuous monitor measurements in Table 4-45. The results in the tables can be used to evaluate waste feed rates, inleak air potential, and ultimately combustion chamber residence times and O_2 concentrations.

The calculated values for stack concentrations in Table 4-45 act as a check on waste feed analysis and waste feed flow rate. In general, the calculated values are close to measured concentrations. For Mitchell and Du Pont, the calculated concentrations always fall outside the range of measured concentrations. These differences may result form a nonrepresentative C to H ratio, or inaccurate waste feed flow rates may have been used.

The two plants physically most likely to yield a value of zero percent inleak are Zapata and American Cyanamid. Both of these incinerators consisted of a combustion chamber leading directly into a stack. Neither had a control system nor extensive ductwork to allow a large amount of inleak to occur. The inleak values for Zapata are all within 10% of zero. Considering the sensitivities discussed above, the calculated values are in good agreement with measured values. American Cyanamid yields large negative numbers for inleak in Runs 2 through 5. This would actually indicate an "outleak" of air from the system between the combustion chamber and the stack. A more likely explanation for these large negative values as well as the difference between Run 1 and Runs 2 through 5 is the location of the thermocouple. The thermocouple at American Cyanamid was located in the uninsulated stack, 3 ft downstream from the combustion chamber. Between Run 1 and Run 2, a flow straightener was installed just below the thermocouple. A temperature difference was measured between Runs 1 and 2 with no accompanying change in operating conditions. These factors combine to indicate an unrepresentatively low temperature reading for Runs 2 through 5. The heat balance calculations show that if the combustion chamber temperature was actually 300°F higher in Runs 2 through 5 (a reasonable assumption based on the temperature differences between Runs 1 and 2), the inleak numbers would be close to zero (±5%). In addition, the O_2 and CO_2 concentrations calculated for the stack would fall within the measured ranges.

TABLE 4-44. VALUES FROM HEAT BALANCE CALCULATIONS[a]

			Calculated values for combustion chamber					Values based on stack measurements		
Plant	Run No.	Chamber temp (°C)	% O_2	% CO_2	Flow rate (dNm³/min)	Residence time (sec)	% Excess air	Flow rate (dNm³/min)	Residence time (sec)	Calculated inleak (as % of stack flow)
Ross	1	1,154	5.2	12.0	530	8.9	34.0	816	6.2	35.1
	2	1,146	4.0	13.0	453	10.3	24.3	789	6.5	42.6
	3	1,117	6.4	11.1	562	8.7	45.0	776	6.7	27.6
Plant B (inlet)[b]	1	1,074	4.6	12.6	126	10.4	28.5	207	6.5	39.1
	2	1,082	4.5	12.8	135	9.3	28.2	195	6.1	30.8
	3	1,056	2.9	14.2	113	11.0	16.2	191	6.2	40.8
Plant B (outlet)[c]	1	1,074	4.6	12.6	126	10.4	28.5	230	6.5	45.2
	2	1,082	4.5	12.8	135	9.3	28.2	227	6.1	40.5
	3	1,056	2.9	14.2	113	11.0	16.2	218	6.2	48.2
	4	879	2.5	14.6	108	13.1	13.9	236	5.9	54.2
	5	968	6.0	11.0	169	8.4	40.1	226	6.5	25.2
Zapata	1	854	12.1	5.8	20.9	0.077	144	21.2	0.069	1.4
	2	867	12.8	5.9	23.0	0.068	171	21.7	0.067	-6.0
	3	844	12.2	5.8	24.3	0.065	148	22.1	0.066	-10.0
	4	904	11.5	6.3	22.0	0.068	127	22.0	0.063	0
American Cyanamid	1	779[d]	13.4	5.4	63.5	0.18	194	66.0	0.17	3.9
	2	671[d]	14.6	4.5	79.3	0.16	257	58.6	0.21	-35.3
	3	629[d]	14.9	4.2	74.2	0.18	278	56.1	0.24	-32.3
	4	648[d]	13.2	6.0	72.3	0.17	189	58.1	0.23	-24.4
	5	679[d]	14.8	4.3	73.7	0.17	271	57.0	0.21	-29.3
Mitchell	1	1,053	4.3	12.2	52.7	3.3	25.0	73.1	2.5	27.9
	2	1,066	6.8	10.2	59.8	3.0	47.9	75.9	2.4	21.2
	3	1,094	7.3	9.8	72.0	2.5	54.6	84.4	2.2	14.7
	4	1,080	5.8	11.0	61.5	2.9	38.6	83.9	2.2	26.7
Du Pont	1 LI	1,450	5.3	11.7	107	0.36	34.0	368[e]	0.226	22.0[e]
	K	1,000	10.8	7.2	180	4.0	112		3.9	
	2 LI	1,450	5.5	11.5	109	0.35	35.9	374[e]	0.228	23.5[e]
	K	975	11.0	7.1	177	4.2	117		4.0	
	3 LI	1,450	5.4	11.8	106	0.36	34.5	385[e]	0.234	22.3[e]
	K	967	11.2	7.1	193	3.9	120		4.2	
TWI	1	1,110	3.1	13.2	55.3	6.4	17.8	108	4.7	48.8
	2	1,090	7.2	9.9	80.2	8.5	53.2	143	3.5	43.9
	3	1,110	7.8	9.3	90.1	5.8	59.4	145	3.5	37.9
	4	965	8.9	8.4	90.4	6.6	78.6	169	3.0	46.5

[a] All values on dry basis except residence times.

[b] Stack flow measured at inlet to scrubber system.

[c] Stack flow measured at outlet from scrubber system.

[d] These temperatures were measured using a thermocouple located 3 ft downstream from the combustion chamber and may be nonrepresentative.

[e] Based on combined flow rate from both combustion chambers.

LI = Liquid injector incinerator.

K = Kiln.

TABLE 4-45. COMPARISON OF STACK CONCENTRATIONS[a]

Plant	Run No.	% Oxygen			% Carbon Dioxide		
		Orsat	Continous monitoring	Calculated	Orsat	Continous monitoring	Calculated
Ross	1	11.5	10.4	10.4	7.1	7.9	7.8
	2	11.7	10.8	10.8	6.9	8.3	7.5
	3	11.1	10.7	10.2	7.3	8.1	8.0
Plant B (inlet)	1	10.3	-	10.6	10.7	-	7.7
	2	10.0	-	9.3	12.0	-	8.9
	3	8.7	-	9.8	10.2	-	8.4
Plant B (outlet)	1	12.7	11.8	11.5	5.1	6.7	6.9
	2	9.9	10.3	10.8	7.7	8.2	7.6
	3	-	10.7	11.1	-	8.0	7.3
	4	15.7	14.3	12.0	5.8	4.8	6.7
	5	12.3	10.1	9.5	8.5	8.1	8.3
Zapata	1	13.3	8.2	12.2	5.8	-	5.7
	2	12.1	12.0	12.8	6.6	-	5.9
	3	11.2	11.8	12.2	6.5	-	5.9
	4	11.1	11.9	11.5	6.7	-	6.3
American Cyanamid	1	12.4	10.3	13.7	6.6	8.8	5.2
	2	14.7	12.4	14.6	4.9	6.8	4.5
	3	14.6	-	14.9	5.0	-	4.2
	4	13.7	12.7	13.2	6.7	7.7	6.0
	5	14.4	13.0	14.8	5.2	6.1	4.3
Mitchell	1	10.5	9.4	8.7	7.8	8.5	8.8
	2	10.8	10.5	9.6	7.7	7.6	8.1
	3	10.1	9.9	9.2	8.4	8.1	7.2
	4	10.6	10.8	9.6	7.9	7.4	8.1
Du Pont	1	9.8	9.2	11.2	8.6	9.2	6.9
	2	10.6	9.6	11.6	8.0	9.0	6.7
	3	10.0	10.3	11.6	8.6	9.0	6.8
TWI	1	14.0	12.4	11.4	5.1	6.6	6.8
	2	13.9	13.0	12.8	5.5	5.5	5.6
	3	13.2	13.2	12.4	5.6	6.1	5.8
	4	15.5	15.6	14.0	4.1	3.9	4.5

[a] All concentrations on a dry basis.

- No data recorded.

The results from the heat balance calculations for all runs at Ross, Plant B, Mitchell, Du Pont, and TWI are also presented in Table 4-44. Values for Upjohn were not calculated because an accurate ultimate analysis of the gaseous feed is not available. For these plants, data in Table 4-44 show that the calculated flow rates are always lower than the stack flow rates. These results suggest that actual residence time may be higher than that estimated based on stack flow but that chamber O_2 concentrations may be considerably lower than the values measured in the stack.

Two sets of residence times are presented in Table 4-44. The values that are based on stack flow are generally lower than those from the heat balance calculation. Since the entire incinerator system operates at a negative pressure, the stack flow represents the highest flow rate at any point in the system. Therefore, residence times calculated using this flow rate probably represent the lower end of the range. Based on the conservative heat loss estimate and the enthalpy values used, the residence times determined by the heat balance calculations are probably near the upper end of the range.

The positive values for percent inleak in Table 4-44 range from 0 to 55%. This inleak could be explained at some plants where visible gaps in the ductwork first raised a concern about inleak of air after the combustion chamber (e.g., TWI). At the more controlled and better maintained facilities, the large inleak numbers are hard to explain. While the leaks in those systems could be significant, the heat balance calculations also may be inexact as described earlier.

The residence time and flow rate values presented in Table 4-44 supplement the numbers in the Appendices C through J. The calculations do show that a significant amount of air may be entering some systems downstream from the combustion chamber. This inleak could be affecting the measured concentrations in the stack, and concentrations of O_2 in the combustion chambers may be lower than the concentrations measured in the stack. For the purpose of data analysis, the residence time numbers based on measured stack flow rates have been used. The calculations do show that the residence times based on stack flow rate are conservatively low for Ross, Plant B, and TWI.

The difficulties encountered while conducting these calculations reflect the uncertainties in temperature and flow rate measurements. Because of these uncertainties caution is recommended whenever viewing plant to plant comparisons based on process parameters involving temperature and chamber flow rate.

4.3.3 Data Handling and Reduction

In addition to the extensive sampling and analysis activities, the trial burn process involves a number of data handling and reduction activities. The evaluation of incinerator performance based on the DRE for specific POHCs has particularly intensive data reduction activities that normally involve several persons. These activities range from calculation of POHC loadings in waste feed samples and sample traps by the analytical chemist based on mass spectrometer output, to the ultimate calculation of DRE by the scientist or engineer with a number of intermediate steps.

The eventual quality of the performance evaluation depends on the use of appropriate procedures and on accurate calculations. The data reduction activities on this program suggest the following:

- The procedure for going from raw data to final DRE as well as procedures for intermediate calculations are not standardized. To insure representative and consistent results, well-defined standard procedures must be developed and used for all calculations.

- Because errors in calculations have just as significant an impact on the final result as sampling and analysis errors, quality control of calculations is imperative.

- Because the final results involve a sequence of calculations, often performed by several individuals and identification and correction of calculation errors can affect subsequent calculations, consistent and accurate results can only be obtained if an organized system of data custody is developed and used.

To ensure data quality on this program, engineering calculations were checked by a second individual, and discrepancies in results were rectified. A single individual was assigned responsibility for maintaining data in notebook(s) for each incinerator test and monitoring the data to insure that changes were carried through subsequent calculations.

In addition to these general procedures, one specific procedure, blank correction for POHCs for the VOST method, was found to be particularly important in reducing the data from the eight incinerator tests. This procedure is discussed in the paragraphs below.

Because achievement of 99.99% DRE often results in stack concentrations that are at or below ambient or laboratory levels for POHCs, contamination of samples can be a significant problem. The purpose of blank correction procedures is to minimize poor decisions based on data from potentially contaminated samples.

The underlying philosophy of the procedure is based on a paper prepared by the American Chemical Society Committee on Environmental Improvement (ACS)[9] and the experience in conducting and interpreting trial burn data from this program. The ACS paper assumes that blank values are random samples from a population distribution that vary because of preparation, handling, and analysis activities. Under this assumption, blank values should be treated statistically. The "best estimate" for the blank for any particular sample is the mean of the population distribution which can be estimated by the mean of the available blanks. The ACS procedure also enables determination of whether a sample is "different from" the blank. If the sample value is not significantly different from the blank value, a sample cannot be blank corrected. However, the measured sample value does provide an upper bound for the emission value. For a trial burn this upper bound may provide sufficient information for decision making; i.e., a greater than value for DRE.

While the procedure outlined by ACS is appropriate if available blank values are random, it is not sufficient if the blanks, and hence samples, are subject to systematic contamination due to sampling conditions. To detect such contamination, the procedure makes use of trip blanks and field blanks. Trip blanks are prepared and analyzed in the same manner as samples. However, they remain in the truck or van throughout the test and are not opened during the test. The field blanks follow the same path as the samples and are exposed to atmospheric conditions during the time the samples are exposed.

If samples are contaminated from exposure during the test, the field blank associated with a specific sample provides a better estimate of the contamination to which the sample has been subjected and should be used as the blank value. Sufficient data were not generated to develop a procedure for determining whether the sample value is "different from" the blank value in these cases, since this situation did not occur during the eight tests.

The procedure does not specify maximum allowable contamination of blanks. However, based on the test conducted on this program proper preparation, handling and analysis of blanks should produce results comparable to those in Table 4-46. Should both trip and field blanks have substantially higher levels of contamination, the usefulness of the data is limited. While the procedures do not preclude the use of data collected under these conditions, the probability that the samples must be treated as upper bounds is quite high. The result may frequently be a lower bound DRE that does not demonstrate that 99.99% has been achieved (e.g., DRE $\geq$ 99.95%).

The proposed blank correction procedure for VOST is:

1. At a minimum one pair of field blanks and one pair of trip blanks should be used for each run during a trial burn. If funding permits, two pair of field blanks and two pair of trip blanks per run are preferable.

2. After all blanks are analyzed, the paired t-test can be used to determine whether the trip blanks are significantly different from the field blanks. If no difference is found (which was the case with all eight tests during this program), the mean and standard deviation of combined trip and field blank values for each compound of interest should be calculated. The mean is used as a blank value for all samples collected during the trial burn. If a difference between the trip and field blanks is found, the field blank (or the mean of multiple field blanks) associated with a particular run should be used as the blank value for that run.

TABLE 4-46. REPRESENTATIVE BLANK LEVELS OBTAINED

Compound	Mitchell		Compound	Du Pont		Compound	TWI	
	Range (ng)	(No. ND/ No. Blanks)		Range (ng)	(No. ND/ No. Blanks)		Range (ng)	(No. ND/ No. Blanks)
Methylene chloride	ND (< 1) - 11	6/10	Methylene chloride	ND (< 2) - 17	1/18	Methylene chloride	1.8 - 64	0/10
Chloroform	ND (< 1) - 2.2	3/10	Chloroform	ND (< 1) - 3.6	8/18	Bromochloromethane	ND (< 1)	10/10
1,1,1-Trichloroethane	ND (< 1) - 4.7	9/10	1,1,1-Trichloroethane	ND (< 1) - 2.1	17/18	Chloroform	ND (< 1) - 12	3/11
Carbon tetrachloride	ND (< 2)	10/10	Carbon tetrachloride	ND (< 2)	18/18	Methylene bromide	ND (< 1)	11/11
Trichloroethylene	ND (< 1) - 1.4	7/10	Trichloroethylene	ND (< 1) - 1.6	12/18	1,1,1-Trichloroethane	ND (< 1) - 7.4	8/11
Benzene	ND (< 3) - 12	9/10	Benzene	ND (< 3) - 21	8/18	Carbon tetrachloride	ND (< 2) [24] [a]	11/11
Tetrachloroethylene	ND (< 1) - 4.1	4/10	Tetrachloroethylene	ND (< 1) - 6.9	13/18	Bromodichloromethane	ND (< 2)	11/11
Toluene	ND (< 2) - 19	1/10	Toluene	ND (< 1) - 14	7/18	Trichloroethylene	ND (< 1) -7.6[36][a]	6/11
Chlorobenzene	ND (< 1) - 2.0	7/10	Chlorobenzene	ND (< 1) - 4.3	5/18	Benzene	4.1 - 38	0/11
			Bromodichloromethane	ND (< 1)	18/18	Dibromochloromethane	ND (< 2)	11/11
			Dibromochloromethane	ND (< 1)	18/18	Bromoform	ND (< 2) - 38	8/11
			Bromoform	ND (< 1)	18/18	Tetrachloroethylene	ND (< 1) - 1.1	6/11
			cis-1,4-Dichloro-2-butene	ND (< 1)	18/18	Toluene	ND (< 2) - 26	4/11
						Chlorobenzene	ND (< 1) - 3.7	10/11

[a] High value on the back trap only on Run 2 suggest contamination during preparation. As a result, this value is not considered representative for a well cleaned trap.

ND - Not detected.

3. For each sample/compound combination, a determination should be made as to whether the sample is "different from" the blank. If the mean of the trip and field blanks is used as the blank, a sample is different from the blank if:

(Measured Sample Value) (ng) - (Average Blank Value) (ng) ≧ 3 x Blank Standard Deviation

(Data were insufficient to develop a procedure for the case where individual field blanks are used as blank values.)

4. If the sample is "different from" the blank, the value used to calculate emission rate and subsequently the DRE is:

Emission Value (ng) = Measured Sample Value (ng) - Blank Value (ng) (as defined in Item 2).

5. If the sample is not "different from" the blank, the measured sample value is used to calculate an upper bound emission value and lower bound DRE, i.e., the emission value is treated as less than or equal to the measured value.

4.4 SAMPLING AND ANALYSIS CONSIDERATIONS

Sampling and analysis procedures for hazardous waste incinerator emissions, and specifically trial burns for these incinerators, are still in a developmental stage. As a result, both sampling and analysis methods are in a state of flux with new procedures being developed and old procedures being modified on a continuing basis.

This program involved trial burn type tests at eight different hazardous waste incinerators. Each test site was unique with wide variations among the eight incinerators in terms of size, design, and complexity. Consequently, the sampling and analysis involved different situations with the use of different procedures as appropriate for each situation. These different situations provided a good testing ground for the evolving S&A procedures.

This section presents a summary of the unique results specifically related to sampling and analysis activities. This program was not a methods development program, and the results presented below do not have the rigorous basis that would be expected for methods development. Consequently, they should be viewed only as input for subsequent methods development programs. Further, the results presented in the section only address a limited number of issues specific to these programs; they do not provide a comprehensive analysis of the sampling and analysis protocol for trial burn testing.

This section is divided into three parts. The first addresses sampling considerations, the second addresses analysis considerations, and the third compares three alternate methods used in this program for volatile organics sampling and analysis.

4.4.1 Sampling Considerations

Sampling during a trial burn generally includes process monitoring, sampling waste feeds, stack sampling for particulate, chlorides and organics, and sampling of other effluent streams. Each of these activities is discussed below.

4.4.1.1 Process Monitoring--

Process monitoring was conducted during each test. This monitoring involved recording all available process instrument readings at specific intervals (e.g., every 30 min) during each run. Also, it involved measuring waste feed tank levels and solids feed data which are essential to determining waste feed rates during each run and, ultimately, to calculation of destruction and removal efficiency (DREs) for each principal organic hazardous constituent (POHC) contained in the waste feeds. Three specific process monitoring problems were identified during this program: (a) determining waste feed rates; (b) spiking liquid feeds; and (c) ascertaining and monitoring key incinerator operating parameters.

Accurate waste feed rates are critical to calculating DRE. In this program, liquid waste feed rates were based on measurements of feedtank levels before, after, and during each test. Data from feed flowmeters at most plants were also recorded and crosschecked with the feed rates determined from tank level changes. The tank level measurements are considered the most reliable and accurate method of determining feed rates because it is impractical to achieve a true calibration of the flowmeters in the field.

Measurement of gaseous waste feed rates is frequently more difficult than measurement of liquid waste feed rates. Only one plant tested in this program had a gaseous waste feed, and the feed rate had to be based on the plant's gas flowmeter. Readouts from gaseous flowmeters (scfm) are usually based on a specific temperature and pressure, and must be corrected if the pressure and temperature are different than those specified in the instrument data sheet (e.g., orifice data sheet).

None of the plants tested in this program continuously fed solids, but some fed solids intermittently in drums. In these cases, preweighing and numbering of all drums was determined to be the most practical method to measure the solid waste feed rate. This procedure necessitated recording the drum number and weight for each drum fed during each test. (Sampling of drum feed under these conditions is discussed in a later section.)

Spiking of hazardous organic constituents in liquid feeds is an accepted trial burn procedure. During the tests at five of the eight sites, a 50/50 mixture of CCl_4 and TCE was continuously pumped (spiked) into the liquid organic waste feed line. The purpose was to obtain DRE results for these two compounds for different incinerators operating at different conditions.

Sampling of the organic waste feed was always done at a point downstream of the spiking point. Analysis results for those samples indicated that the concentrations of CCl_4 and TCE were sometimes one-third to one-half of the expected concentration calculated from the spiking rate and waste feed rate. Investigation of this problem indicated that the most likely cause was poor mixing of the spiking solution with the waste feed. Prior to the tests at the last plant (TWI), in-line mixers were installed in the waste feed line between the spiking point and the sampling point. Results of this test showed good agreement between the concentration determined by analysis of the liquid waste feed samples and that calculated from the spiking rate. These results suggest that in-line mixers may be needed whenever compounds (POHCs) are to be continuously spiked into a waste feed line.

Trial burn type tests usually are intended to assess performance of the unit operating at or near design conditions. Prior to the trial burn, acceptable ranges for key design or operating parameters must be defined, and it must be ascertained that the parameters can be monitored during the test.

One design aspect which should be investigated by the process monitor before starting the test is burner turndown ratio. DRE can be adversely affected when operating at high turndown rates. Liquid injection burners are designed to handle a certain liquid flow rate and usually have a manufacturers recommended turndown ratio. For example, a burner may be designed for a flow of 30 Lpm, with a maximum recommended turndown ratio of 3:1 (i.e., 10 Lpm). If, for some reason, the tests were carried out when feeding only 3 Lpm, the burner atomization and resulting DRE could be adversely affected.

It is also essential to determine that an instrument is actually measuring what one thinks it is measuring; labels can be deceiving. For instance, a flowmeter may be located in a feedline, with a downstream recirculation line back to the feed tank. Thus it does not measure feed rate to the incinerator, even though the label may imply that it does. Physical inspections and tracing of lines and instruments with operator assistance, is highly recommended to help avoid these situations.

4.4.1.2 Waste Sampling--

One of the major concerns in this project was composition variability of waste used throughout each test and use of appropriate techniques for representative waste feed sampling. Some of the results of this program pertaining to waste feed variability and sampling are presented below for both liquid and solid waste feeds.

As in earlier tests conducted at the Cincinnati MSD incinerator, tests conducted in this project showed that liquid wastes sometimes vary in composition within any one run. Such variations were observed even in cases where a feed tank was equipped with a mixer and/or was continuously recirculated. The clearest indication of this variability was from process observations. During very stable operation, temperatures would begin to rapidly increase (or decrease) and instrumentation would automatically adjust liquid waste feed rate. Since the increase occurs without any indication on any other instruments that other parameters might have caused the increase, the waste feed composition (e.g., heating value) had probably changed. Such changes indicate stratification in the waste feed tank.

Because of such observations, frequent sampling of the liquid waste feeds during each run to form a composite sample was necessary. (Continuous sampling was not feasible for these feeds.) Subsamples were normally taken every 15 min as the shortest practicable interval.

One finding related to the waste feed sampling was that great care must be taken in sampling from the liquid organic waste feed lines. When each subsample is taken, the sample tap must be opened long enough to clear out liquid trapped in the sampling line so that the subsample is representative of the liquid flowing in the feed line. However, the draining and sampling from this tap must be done slowly and carefully so that the flow of waste to the burner is not greatly affected, or that no automatic shutdown systems (e.g., low waste feed pressure) are activated. In addition, personnel must be supplied with proper safety equipment and employ appropriate safety procedures during sampling.

At one plant (Zapata) sampling directly from the waste feed line to the burner was not possible. Each subsample was taken from a drain line in the bottom center of a very small waste feed tank (~ 280 L capacity), which was near the pump suction line in the side of the tank. This sampling point appeared to be satisfactory during the first run. On subsequent runs, after additional waste was put into the feed tank, some of the subsamples had a high water content. These samples were probably not representative of the feed to the incinerator since it continued to operate without any indication that the feed might be high in water content. To avoid such sampling problems waste feed samples should be taken from the waste feed line to the incinerator whenever possible.

No continuously fed solid streams were included in this project, but some sites did involve drummed material fed intermittently. Drummed materials were usually solids or semisolids but in some cases included liquids alone or multiphase liquids and solids. Solids also included anything from actual solids to glue-like material. As a result, many different drum sampling methods were employed.

An attempt was made to always sample every individual drum, but in some cases several drums contained similar or identical waste. In those cases, the samples from drums of similar types of waste were composited. This procedure is reasonably easy if each drum can be sampled as it is fed to the incinerator. At one site, where sampling just prior to incineration was not feasible, all drums were sampled before testing. A record was kept of the drums fed to the incinerator during the actual test period, and samples from appropriate drums were composited, after completion of the testing.

One conclusion from these waste sampling activities was that the composite liquid waste sampler (Coliwasa) should be modified, because it was difficult to use, frequently did not seal properly, and obtained too large a sample. A modified Coliwasa was developed (see Figure 4-12) that eliminated the above problems. This modified Coliwasa provides a positive seal at the bottom (a ball valve), and provides a smaller sample size. It also is still usable through the bung hole in the lid of the drum(s).

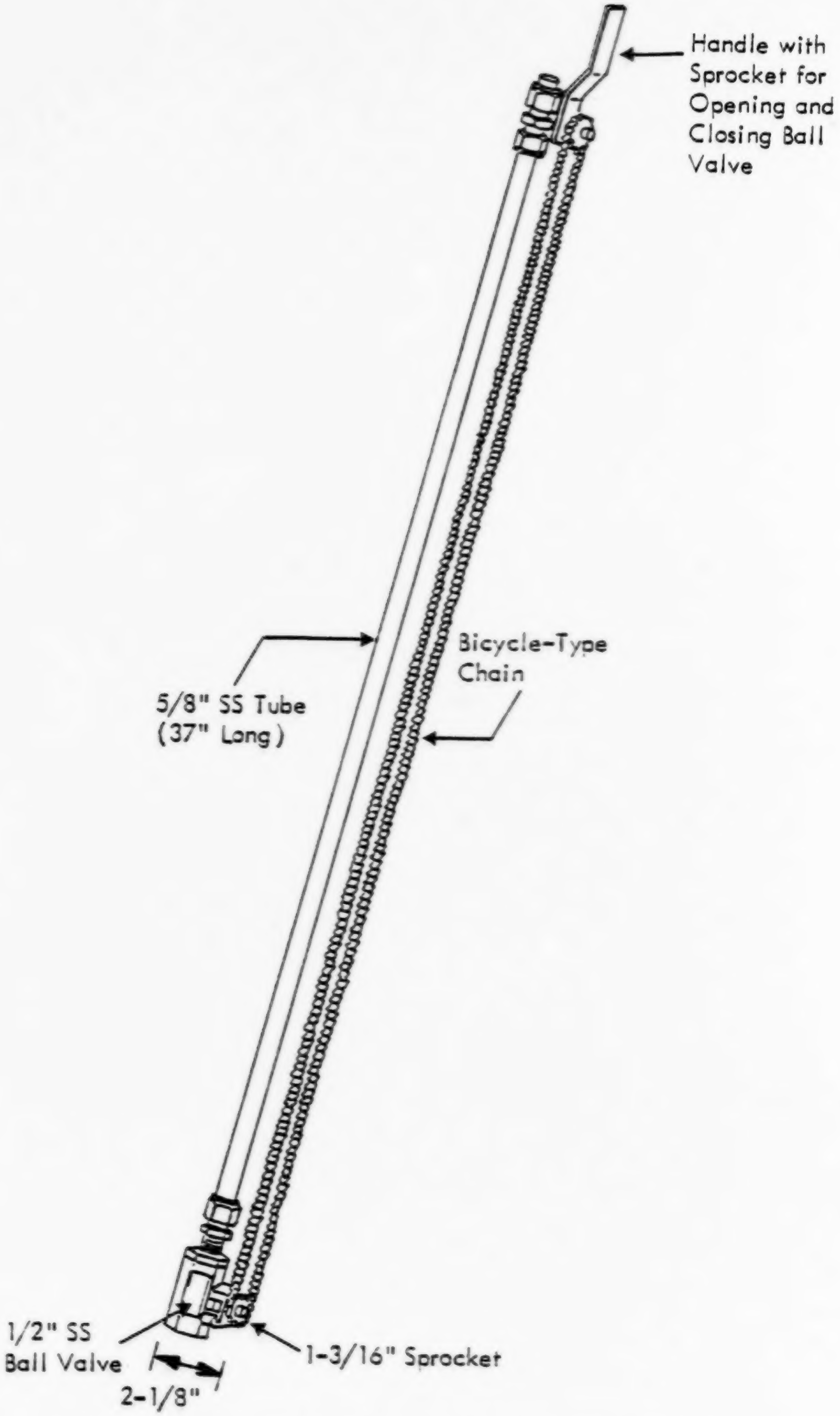
Handle with
Sprocket for
Opening and
Closing Ball
Valve
Bicycle-Type
Chain
5/8" SS Tube
(37" Long)
1/2" SS
Ball Valve
1-3/16" Sprocket
2-1/8"

Figure 4-12. Diagram of modified Coliwasa.

4.4.1.3 Stack Effluent Sampling--

One of the key elements of an incinerator trial burn is sampling the stack effluent for volatile and semivolatile organics, particulates, and chlorides. Most of the significant sampling considerations from this program were associated with the organic sampling. Major issues were detection limit considerations, blank problems, and cleanup procedures. The other major problem addressed in the study was cyclonic stack flow. Each of these issues is discussed in the subsection below.

4.4.1.3.1 Detection limit considerations--Results of this and other programs have shown that 1 μg of each semivolatile POHC should be collected in a MM5 train to be detectable in the subsequent GC/MS analysis of the combined extract of the MM5 train components. At a POHC concentration in the stack effluent of 1 $\mu g/m^3$ (1 ng/L), the MM5 sampling rate of 1 m^3/hr and sampling time of 2 to 3 hr provides enough of the POHC (2 to 3 μg) to be above the detection limit (1 μg). Detection of 1 $\mu g/m^3$ of a POHC in the stack effluent will demonstrate that a DRE of 99.99% is achieved for an incinerator burning a waste containing 100 μg/g (100 ppm) or more of a POHC. If the concentration of the POHC in the stack effluent is much higher than 1 $\mu g/m^3$ because of a DRE below 99.99% or because of a much higher concentration in the waste feed, no problems are created since the extract can always be diluted and reanalyzed.

While an extract may be simply diluted and reanalyzed in the case of semivolatiles, the situation is not so simple for analysis of volatile POHCs. The method for analysis of volatile POHCs was designed to be able to quantify volatile POHCs so that a DRE of 99.99% is measurable at the 100 μg/g level of a POHC in the waste. The VOST method samples 20 L of stack effluent through each pair of traps. If the sample contained 1 ng/L of a POHC (as discussed above) the amount contained on any one pair of traps (or on one of the two traps) would be 20 ng, which is well above the detection limit of about 2 ng. However, analytical problems may arise when analyzing samples from incineration waste feeds with very wide range of concentration of POHCs. For example, if the concentration of a POHC in the waste were 100,000 μg/g (10%), the resulting POHC concentration in the stack effluent would be 1,000 ng/L if the incinerator was achieving a DRE of exactly 99.99%. In this case the amount of POHC caught on any one pair of traps is 20,000 ng.

During thermal desorption the entire collected sample enters the GC/MS and would very likely saturate the MS detector. When this saturation of the primary characteristic ion occurs, as happened in a few cases in this program, the only alternative available is to perform the quantitation based on one of the minor fragmentation ions. When this technique is used, the results may not be as accurate as when the quantitation is based on the primary characteristic ion for the specific POHC.

During this program quantification of POHCs based on one of the minor fragmentation ions was not a widespread problem. Since compounds present in the waste at high concentrations generally had higher DREs (see Section 4.1), either the emission rate could be quantified without saturating the MS or the compound achieved the 99.99% DRE standard by such a wide margin that measurement inaccuracies were not a problem. However, in a few cases for which benzene and toluene were quantified by minor ions, the inaccuracy of the method may have resulted in an incorrect determination of achievement of 99.99% DRE.

An alternative for quantifying high concentration POHCs is to sample with gas bags or gas bulbs (glass) and analyze much smaller sample volumes (e.g., 1 mL) by direct injection into the GC or GC/MS or by concentrating a smaller portion of the sample on a VOST trap (e.g., 5.0 L). If such samples also contain low concentration POHCs (a common situation), neither VOST or gas bags alone can adequately quantitate both the low and high concentration POHCs, and both types of analysis would be necessary. Since prediction of concentrations of POHCs in samples is difficult, collection of both VOST and gas bag samples may be advisable.

4.4.1.3.2 Blank requirements--Blanks are an extremely important part of the sampling and analysis, both for quality assurance and for evaluating the results. Particulate measurement requires probe rinse reagent blanks and filter blanks to properly correct the final results. Blanks are perhaps even more important to quantify POHCs.

Modified Method 5 is used to quantify particulate emissions and semivolatile POHCs. The probe rinse reagent blanks and filter blanks serve a dual purpose as blanks for both particulate and semivolatile POHC measurement. A blank XAD resin trap is also required for POHC measurement. All three of the above MM5 component blanks must be extracted and the extracts combined and analyzed. The analysis result for the blanks can then be used to correct the sample results, if the amount of the POHC in the samples is "significantly" greater than any amounts found in the blanks. In this program, the results were blank corrected if the sample amount was more than three times any blank amount. If not, the entire sample amount was used as the result and expressed as a "less than" value with the resultant DREs expressed as a "greater than" value. Frequently the POHC levels in both the samples and blanks were below the detection limit resulting in a "greater than" DRE. In some cases, both the sample value and blank value were high, resulting in a greater than value for DRE which was below 99.99% (e.g., > 99.98%). This result does not show that the desired DRE of 99.99% was achieved.

Procedures developed in this project required two pairs of VOST blanks for each run (three runs per test site). For each run, one pair of traps served as a trip blank and one pair as a field blank. The only difference in these blanks is that trip blanks are never opened in the field whereas the field blank pairs are taken up on the stack and opened to the ambient air for about the same period of time that an actual sample pair is open to the ambient air when inserting or removing them from the VOST.

Results from this program for each site showed that trip blanks were statistically not significantly different from the field blanks, indicating that field blanks did not become "contaminated" due to their exposure in the field. It was possible to calculate a mean and standard deviation from the data for combined trip and field blanks per methods described in Section 4.3.3. In several cases VOST samples could not be corrected because both the samples and the blanks were below the detection limit, and the DRE had to be reported as a 'greater than' value.

Tedlar gas bags were used at all eight test sites to collect effluent gas samples continuously over a 1 to 2 hr period during each test. Another Tedlar bag was filled with prepure nitrogen and inserted in the same, or an identical, sampling box as the sample bag and taken up to the sampling platform. After each test, the sample bags and blank bags were returned for analysis.

Blank bag results were extremely important since in many cases the analysis results showed that blanks contained greater concentrations of some POHCs than the concentrations in the sample bags. Bag preparation procedures, and methods of transporting and protecting the samples were investigated. Data collected during this program were not sufficient to define specific causes or methods of prevention.

4.4.1.3.3 Cleanup procedures--Preparations for field testing include many cleanup procedures for sampling equipment, sample containers, etc. Because problems with high blanks for VOST traps occurred when the VOST was first used in the field, extensive cleanup procedures subsequently were implemented that minimized this problem. Those cleanup procedures are specified in Figure 4-13. One of the key steps in the cleanup is purged heating of every trap, with FID analysis of the effluent purge gas from each trap. No trap was considered clean and ready for shipment to the test site unless the FID analysis showed that the effluent purge gas contained less than 5 ppb of total hydrocarbons (based on propane as FID calibration gas). These procedures resulted in significantly reduced levels of blank trap contamination in later tests.

4.4.1.3.4 Cyclonic flow considerations--One of the first steps prescribed for MM5, is a preliminary test to check for cyclonic flow. That procedure was carried out at all of the test sites; cyclonic flow was found at the stack sampling location for two of the sites. At one site the cyclonic flow could be anticipated since the two forced draft fan ducts directed the flow tangentially into the combustion chamber. No reason for cyclonic flow at the other site was noted. In both cases before testing, flow straighteners were fabricated and inserted in the stack several diameters upstream of the sampling location to eliminate the cyclonic flow problem.

The experience on this program shows that cyclonic flow may exist in a stack even when not anticipated. The problem can be eliminated by installation of flow straighteners; but this step can cause considerable delay. Usually the check for excessive cyclonic flow can be done only just prior to the start of testing. If cyclonic flow is found to exceed the EPA limit, a flow straightener must be designed, fabricated, and installed, which will

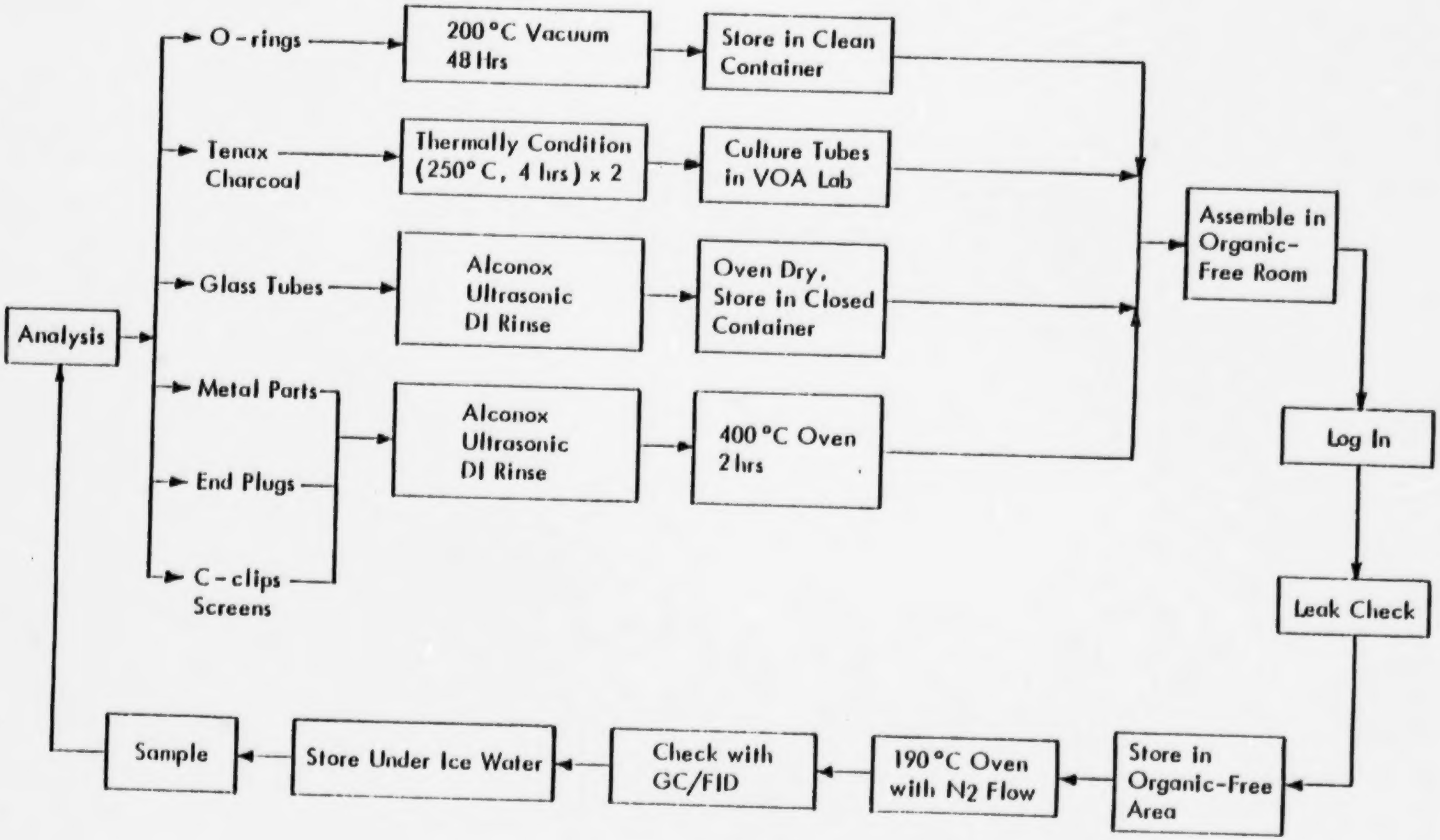
Analysis
O-rings
Tenax
Charcoal
Glass Tubes
Metal Parts
End Plugs
C-clips
Screens
200 °C Vacuum
48 Hrs
Thermally Condition
(250° C, 4 hrs) x 2
Alconox
Ultrasonic
DI Rinse
Alconox
Ultrasonic
DI Rinse
Store in Clean
Container
Culture Tubes
in VOA Lab
Oven Dry,
Store in Closed
Container
400 °C Oven
2 hrs
Assemble in
Organic-
Free Room
Log In
Leak Check
Store in
Organic-Free
Area
190 °C Oven
with N2 Flow
Check with
GC/FID
Store Under Ice Water
Sample

Figure 4-13. Schematic of trap cleanup procedures.

likely require shut-off and cool-down of the incinerator. Fortunately in the two sites tested the work could be accomplished with a delay of only 1 day. However, a delay of several days might be necessary in other situations. If the flow is anticipated to be cyclonic, a flow straightener should be installed in advance of the tests.

4.4.2 Analysis Considerations

As with the sampling procedures described in the last section, analytical procedures for trial burns are still in the development stage. Analyses are complicated by situations in which relatively small levels of hazardous constituents must be extracted and detected in a complex matrix of organic compounds. This problem was particularly noticeable in the analysis of waste feed samples which is described in the first subsection below. Considerations regarding selection of surrogates, metals analysis, and field analysis for POHCs in the stack effluents are addressed in other subsections.

4.4.2.1 Analysis of Waste Feed Samples--

Because of their complex nature, analysis of waste samples presented a number of unique problems. The paragraphs below discuss the following issues related to waste feed sampling: (a) surrogate spiking levels; (b) problems in spiking and extracting aqueous samples; (c) identification of POHCs in waste feeds; (d) use of GC/FID prescreening; (e) difficulties in detecting low level POHCs; (f) use of tetraglyme for extracting volatile POHCs; (g) problems in determining moisture content.

Surrogates used in the analysis of waste feed samples often had to be spiked into the samples without prior knowledge of the POHC concentrations and therefore, without knowledge of any dilution of the samples necessary to quantitate the POHCs. In some cases subsequent dilutions resulted in a surrogate concentration close to or below the detection limit. Those which were above, but relatively close to, the detection limit could be quantified but results in this region are less accurate and may yield recovery efficiencies that are outside the desired range. This problem potentially could be avoided if adequate information about the samples from prior waste characterization data was available, or if an initial analysis could be performed to ascertain the required dilution. Appropriate spiking levels for the surrogates then could be used when the samples are reanalyzed.

Many aqueous samples were collected for analysis of POHCs. QA procedures required that some of these samples be fortified with the POHCs to determine percent recovery (i.e., accuracy). In some instances the total concentration of some compounds (i.e., native concentration plus amount fortified) exceeded the solubility limit. If aqueous samples are to be spiked with any organic compound, the solubility limit of the compound must be considered to determine how much of the compound can be spiked into the sample.

Aqueous samples, such as scrubber effluents, were first extracted for POHC analysis by shakeout in separatory funnels according to EPA Method 625.

However, the separatory funnel shakeout results indicated that better reproducibility and surrogate recoveries might have been obtained if continuous extractors (an option in Method 625) had been used. Use of the continuous extractors is recommended for extracting aqueous samples.

Usually very little prior information was available about POHCs (Appendix VIII compounds) present in the waste feeds so there was no preselection of POHCs. Even when information was available, one objective of the project was to identify and quantitate as POHCs all Appendix VIII compounds that were present at concentrations greater than 100 ppm. Since many of the wastes were complex mixtures that produced many peaks in the GC/MS chromatogram, complete characterization of the waste presented some problems.

An attempt was made to write and use a computerized search routine to identify all the peaks that were Appendix VIII compounds. Because the approach was time-consuming and extensive computer time was required, a manual method was used instead. Experienced staff can expedite the manual search, since familiarity with the mass spectra of many of the compounds allows peaks to be easily eliminated or selected for closer confirmatory scrutiny as Appendix VIII compounds. However, this manual search still requires considerable time by highly qualified and experienced personnel. Also, it is impossible to identify all Appendix VIII compounds because some cannot be determined by GC/MS and require other analytical methods (e.g., formaldehyde).

Analysis of waste feed extracts included prescreening with GC/FID to check the concentration of major components in the extracts. The purpose was to determine if further dilution or concentration of the extract was needed to achieve maximum sensitivity in the GC/MS analysis, but to avoid overloading the GC/MS with major sample constituents. The procedure of prescreening with GC/FID was quite useful for optimizing sensitivity in the subsequent GC/MS analysis and minimizing the number of GC/MS analyses that would otherwise have been necessary. When extracts are diluted, the concentration of the POHCs that were present at low levels in the original sample (e.g., 100-1,000 ppm) will be further diluted, making it more difficult to detect and quantitate those POHCs.

Another problem usually associated with analyzing for POHCs in waste feeds is interferences. That is, the POHC may coelute with a major component, thus making it difficult to detect the presence of that POHC. This same problem can also occur for samples other than waste feeds, but this program identified few instances of interferences in sample types other than waste feed samples (e.g., stack effluent).

A normal procedure used to analyze volatile POHCs in waste feed samples is to disperse an aliquot of the waste in a solvent and analyze it by direct injection GC/MS. However, this procedure can result in the solvent masking some of the POHCs. Also, the direct injection may provide inadequate sensitivity. These potential problems can be minimized by use of an alternate method that has been used and is allowed under the recommended analysis procedures. This method involves dispersing an aliquot of the waste in tetraglyme, which is then dispersed in water and analyzed by purge-trap-desorb (P-T-D) GC/MS. The tetraglyme is a good solvent for the wastes and allows the sample to be dispersed in water for analysis by conventional waste water analysis procedures (i.e., EPA Method 624).

The procedure used to analyze for volatile POHCs in waste feed samples was to disperse 2 g of the homogenized waste in 40 ml of prepurified tetraglyme. An aliquot of the tetraglyme solution was than added to reagent water, along with a known amount of an internal standard. The water was then analyzed by P-T-D GC/MS per EPA Method 624. In some cases, a reanalysis was done using different amounts of the tetraglyme solution in order to optimize the GC/MS response. Use of the tetraglyme in the analysis procedure was very successful and eliminated masking problems that can occur in other methods that involve dispersing an aliquot of the waste in a solvent.

Waste feeds at all test sites (except Upjohn) were analyzed for water content. (At Upjohn, the waste stream's moisture content was assumed to be zero due to the strong reactivity of water with the isocyanates in the waste feed.) Water content varied from 0.43 to 56% in nonaqueous waste streams and 89 to 98% in aqueous waste streams.

Originally, the "Sampling and Analysis Manual for Hazardous Waste Incineration"[10] specified the determination of water content by ASTM Method D-1888-78, which measured weight loss after heating the sample past the boiling point of water. However, this method is not suitable for testing organic materials. Instead, the Karl Fischer titration method was used for all of the water analyses reported in this study. The newest edition of the analysis manual, made available after this test program had commenced, specified ASTM Method D95 which uses xylene extraction and distillation of the water fraction. No data were obtained in this program that would allow comparison of the results of the Karl Fischer titration with Method D95.

4.4.2.2 Selection of Surrogates--

Results from this program showed variable recoveries for the surrogates in all the different types of samples (waste feeds, stack effluents, etc.). This variability made it difficult to use the surrogate analysis results in assessing the POHC results. In particular, the surrogate D_{12}-chrysene often exhibited low recovery. However, this surrogate is a polycyclic hydrocarbon that is dissimilar to most of the POHCs observed in this program.

The most desirable surrogates would be the stable isotopically labeled forms of all, or at least some, of the POHCs of interest. However, the POHCs may not be known until after the waste has been analyzed. The cost and availability of the isotopically labeled compounds also may preclude their use. More investigative work is needed to facilitate appropriate selection of surrogates.

4.4.2.3 Metals Analysis--

The methods used for metals analysis of waste feeds, ash, and particulate are described in Appendix B. Because there is some uncertainty in these procedures, especially with regard to complex waste feeds, investigation and validation of these procedures for widely varied types of waste feed samples is needed.

Particulate samples were analyzed for metals by digestion of the particulate catch on the glass fiber filters. Results indicated relatively high blank levels for many of the metals. This was primarily due to the fact that the particulate weight was quite small compared to the much larger weight of the filter itself. If better metal quantification were required in future projects, much longer sampling times, or possibly different filters, would be necessary.

4.4.2.4 Field Analysis of POHCs--

All of the POHC analysis activity in this program was conducted after samples were returned to the analytical laboratory, except for one additional special analysis activity conducted at the last test site (TWI), as reported in Appendix J. The purpose of this activity was to analyze grab samples of the waste feed and stack effluent for two specific POHCs (CCl_4 and TCE) by GC/ECD in the field. These results were then compared with the normal analysis of samples back at the analytical laboratory. In addition, some of the grab samples were returned to the analytical laboratory for analysis by GC/ECD (waste feeds) and GC/MS (gas sample bulbs).

Key results of this modified sampling program were:

- When the analytical results were compared with concentrations calculated from known spiking rates and waste feed rates, the GC/MS results agreed most closely with calculated rates. The laboratory GC/ECD results were considerably higher than the calculated rates, but the field GC/ECD results were generally lower.
- Gas bulb results as analyzed by both field GC/ECD and laboratory GC/MS were much higher than VOST results. These results are based on the initial attempts to use gas bulbs with field GC/ECD. Further work is needed to explain these results.
- In some cases syringe blank levels were quite high, possibly due to contamination from storage near waste samples.
- In most cases field GC/ECD analyses of gas bulbs yielded higher results than GC/MS analyses, possibly due to interferences from coeluting compounds.

These results suggest that further work is needed before the field GC/ECD method can be utilized with confidence and provide an advantage in rapid evaluation of incinerator DRE performance. Recommended changes and work are noted in Appendix J.

4.4.3 Comparison of Alternate Volatile Organic Sampling Methods

Three different methods of stack sampling for volatile organics were used during this program. Gas bag and VOST sampling were performed at all eight facilities. In addition, VOST was operated at two different sampling flow rates (fast and slow) during the final three tests. This section compares the fast VOST method with the slow VOST and gas bag methods.

The gas bag method involves drawing a sample of stack gas into a Tedlar bag over the duration of the test run (approximately 2 hr) at a flow rate of approximately 50 mL/min. Part of this sample (usually 5.0 L) is transferred in the lab onto a Tenax trap which is then analyzed for volatile organics. Fast VOST is conducted over several 20-min periods during the run. For each 20 min period a pair of adsorbent traps collects sample at a flow rate of approximately 1 L/min. The traps are then returned to the lab for analysis. The slow VOST sampling was conducted at three plants using trains identical to the fast VOST. During the Mitchell and Du Pont tests, the slow VOST was operated simultaneously with the fast VOST train, but at a lower flow rate (250 mL/min). This resulted in a lower total sample volume for the slow VOST. At TWI, each slow VOST trap pair was operated for the duration of two pairs of fast VOST traps (a total of 40 min) at the lower flow rate (250 mL/min). More detailed descriptions of the methods are contained in Appendix B.

The three different methods gave somewhat different results for volatile organic emissions. The test average concentrations measured by each of the three methods during the last three tests are presented in Figures 4-14 to 4-16. These averages are for the seven POHC and PIC compounds which were present in detectable concentrations at all three facilities. These data provide the most complete data set and are used for most of the subsequent comparisons of the three methods.

The two subsections below compare fast VOST to gas bags and fast VOST to slow VOST. As indicated in these sections, the data generated by fast VOST provide the most complete set of quantifiable data generated in this program. Hence, they are the primary data used in the analyses reported in later sections of the report.

4.4.3.1 Fast VOST/Gas Bag Comparison--

The comparison of the fast VOST and gas bag methods focused in three areas: (a) the relative level of incinerator performance as measured by each method; (b) the ability of each method to produce quantifiable emission rates (i.e., the ability to distinguish between sample values and blank values); and (c) the reliability and performance of the alternate methods based on judgments by sampling personnel. As described in the discussion below, differences in assessment of incinerator performance via the alternate methods are minimal, but the fast VOST tends to produce more quantifiable results and have fewer operational problems. Based on the results of these tests, fast VOST appears to be more reliable than the gas bag method.

Two relative measures of incinerator performance were examined--the concentration of specific POHCs in the stack effluent as measured by each method and an assessment of whether the facility achieved 99.99% DRE for a specific POHC. The results of each analysis are described below.

When both the gas bag and VOST results were quantifiable, the concentrations measured by the two methods did not differ significantly. Examination of the data in Figure 4-14 shows that the gas bags gave higher concentrations than fast VOST for six of the seven compounds at Mitchell.

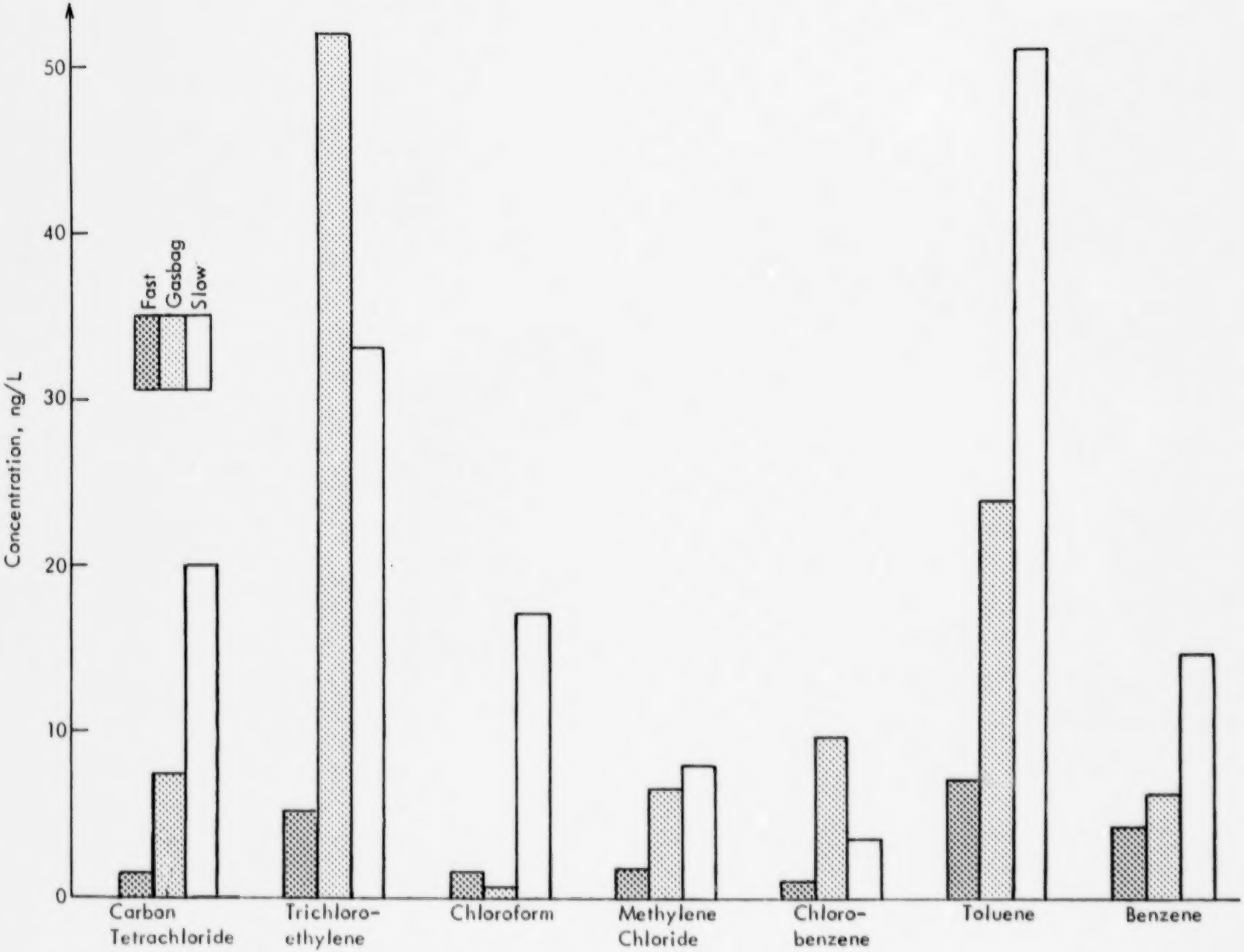

Figure 4-14. Comparison of three volatile sampling methods - Mitchell.

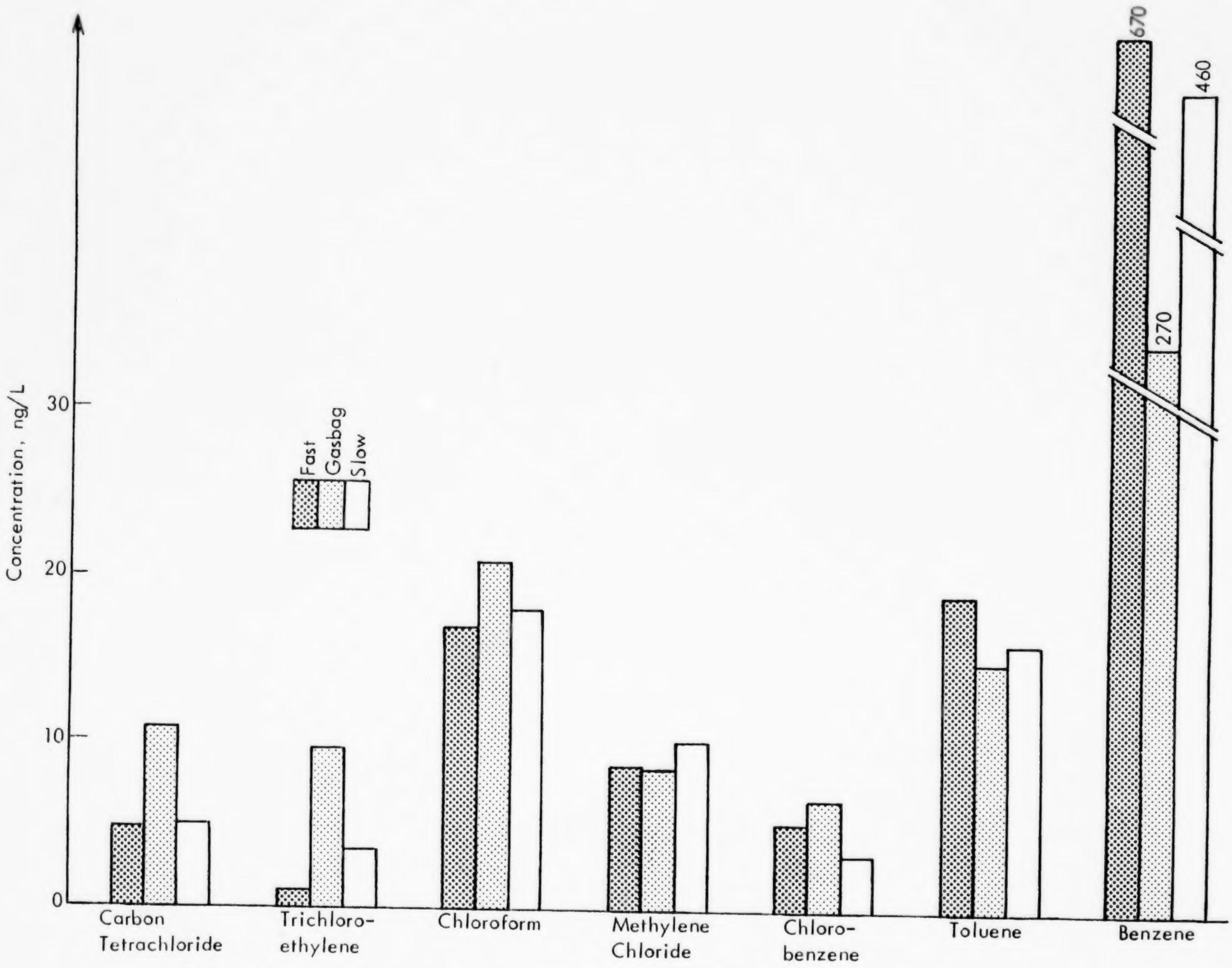

Figure 4-15. Comparison of three volatile sampling methods - Du Pont.

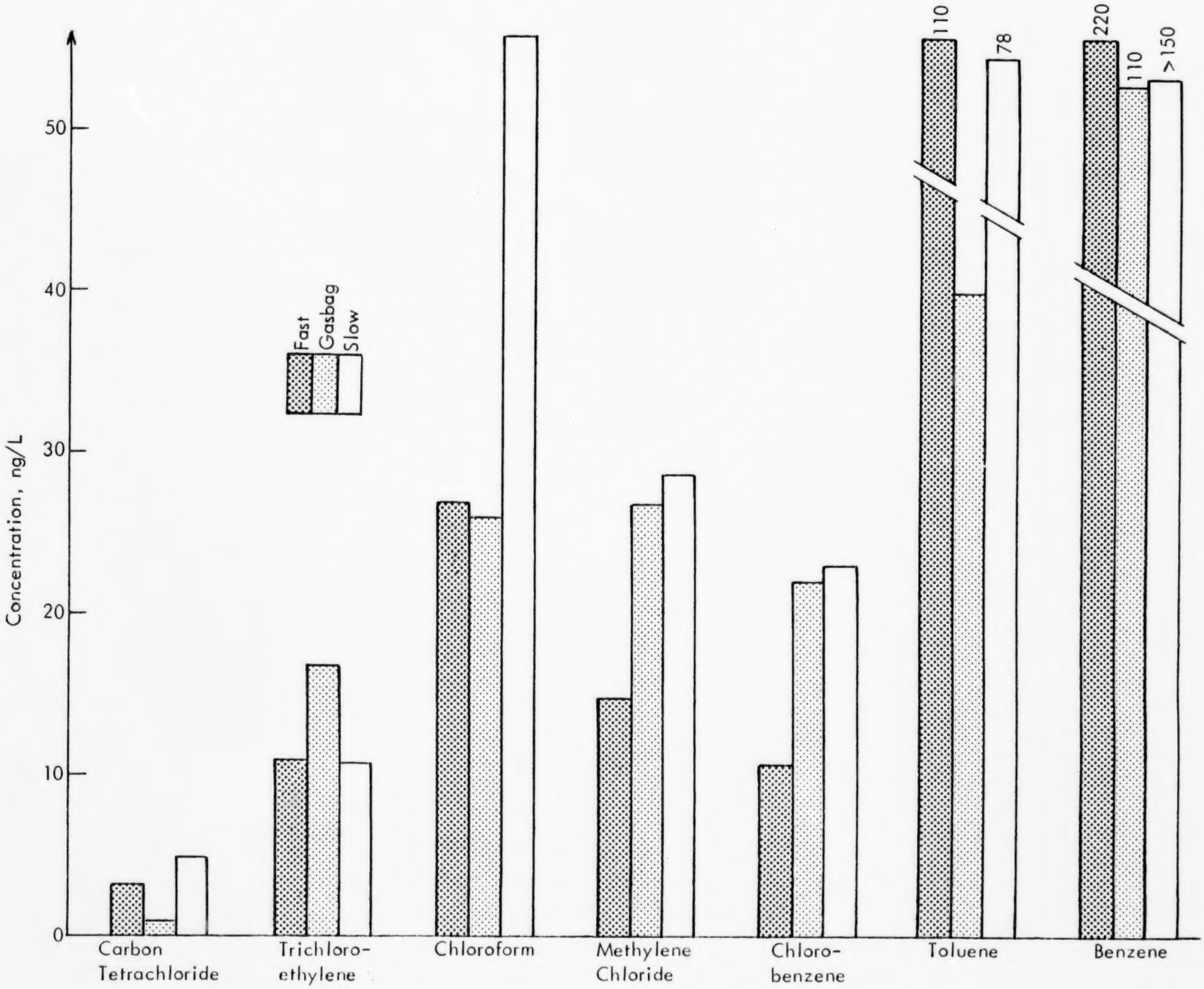

Figure 4-16. Comparison of three volatile sampling methods - TWI.

However, for the other two plants gas bag concentrations fluctuated around the fast VOST concentrations. The only compound which showed any consistent bias in the concentration measured by one method over the other was trichloroethylene which gave a much higher concentration (> 200%) for the gas bag in seven out of the eight runs where it was quantifiable. In examining data statistically by compound for all plants, no significant differences in mean emission concentrations were found.

The sampling method had a mixed effect on determination of DRE, but neither method showed inherent biases. Of the 88 cases during the eight tests where both gas bag and fast VOST had a DRE which was clearly on one side of 99.99%, the methods disagreed 19% of the time. Seven percent of the time the gas bag results indicated achievement of a DRE a greater than 99.99% while the fast VOST did not. Twelve percent of the time the fast VOST results indicated achievement of a DRE a greater than 99.99% while the gas bag did not.

One of the major objectives of a method is the ability to produce quantifiable values. This objective can only be achieved if consistent blank values at a relatively low level can be obtained. Following is a brief overview of the blank values for the tests based on the nine most common volatile compounds.

When the blank values for gas bags and fast VOST are converted to concentrations (using a 5.0 L sample for gas bags and a 20 L sample for fast VOST), the blank data clearly separate the first three tests from the last five. During the first three tests the concentration values for gas bag blanks were lower than those for VOST blanks 86% of the time. For the last five tests the trend was reversed with concentration values for VOST blanks lower than those for gas bag blanks 93% of the time. The primary reason for this difference in values is that improved cleanup procedures for VOST traps evolved over the first three tests. The values for VOST blanks decreased by a factor of 35 or more for seven of the nine compounds when the average for the last five tests is compared to the average for the first three.

The improved VOST preparation procedures produced a very reliable set of data for the fast VOST method over the last five tests. Based on this data set, the VOST method produced only 19 observations which were indistinguishable from blank values (20% of the VOST observations). The gas bags produced 54 observations in which the sample was indistinguishable from the blank (57% of the gas bag observations).

The VOST method produces concentration data for different periods throughout the test run. These variations will expose any changes in incinerator operation during the course of a test run. This phenomenon was most noticeable at Zapata, American Cyanamid, and Mitchell where the measured concentrations of most volatiles tended to decrease as the run progressed. Based on this advantage, fast VOST appears preferable from a sampling perspective.

4.1.3.2 Fast VOST/Slow VOST Comparison--

In comparing fast VOST and slow VOST, little operational difference in the methods were observed. The slower flow rate used with slow VOST does allow the use of fewer traps over a complete test with corresponding ease of sampling and reduced analytical costs. No other operational differences were noted.

Three types of analyses were conducted on the fast VOST and slow VOST results: (a) a comparison of the measured concentrations of the two methods; (b) the determination of the ability of the incinerator to achieve 99.99% DRE; and (c) the relative quantity of POHCs captured on the first and second traps. These results are described below.

The results for the slow VOST are compared with those for fast VOST in Figures 4-14 to 4-16. The Mitchell incinerator produced fast VOST values consistently lower than corresponding slow VOST values. The results at the other two plants varied among compounds. These observations are difficult to explain. The VOST adsorption phenomena are certainly complex, and retention volumes for specific compounds may be dependent on the stack gas composition. If so, this mechanism provides an explanation for the varying behavior of the samples obtained using the VOST. Much more work is needed however, before a definitive explanation of VOST behavior can be developed.

The difference between slow VOST and fast VOST had little effect on DRE calculations. Of the 62 cases at the last three plants where both fast and slow VOST had quantifiable DRE values, the methods disagreed 11% of the time on achievement of 99.99% DRE. Three percent of the time slow VOST results demonstrate achievement of the required DRE and fast VOST did not. Eight percent of the time fast VOST results demonstrated achievment of the required DRE and slow VOST did not.

One parameter that can be used as an indicator of breakthrough due to either trap saturation or excess gas velocities through the trap is the relative contribution of the first trap to the total catch. As shown in Table 4-47, the data from Mitchell, Du Pont, and TWI for the nine most prevalent volatile POHCs showed no consistent pattern either by compound or by plant. Further, the results for fast VOST and slow VOST exhibited no consistent differences with respect to fraction of the POHCs on the first trap. Of the 15 cases which differed significantly, eight had greater first trap fractions on the fast VOST test and seven had greater first trap fractions on the slow VOST test. These results provide no indication of a breakthrough phenomena for either slow or fast VOST.

TABLE 4.47. TRAP DISTRIBUTION IN VOST SAMPLES FOR SELECTED COMPOUNDS

	Front trap catch as % of total catch					
	Mitchell		Du Pont		TWI	
	Fast	Slow	Fast	Slow	Fast	Slow
Methylene chloride	39	49	34	66	71	75
Chloroform	78	48	97	95	89	99
1,1,1-Trichloroethane	85	67	67	100	79	93
Carbon tetrachloride	62	49	67	89	75	92
Trichloroethylene	45	32	73	42	93	88
Benzene	72	72	89	97	94	89
Tetrachloroethylene	89	59	98	94	99	95
Toluene	58	58	96	83	97	96
Chlorobenzene	62	80	88	75	96	98

4.5 REFERENCES

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